

# **The Use of Amalgam Electrodes to Measure Activity Coefficients in Multicomponent Salt Solutions**

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## FOREWORD

This is one of a continuing series of reports designed to present accounts of progress in saline water conversion and the economics of its application. Such data are expected to contribute to the long-range development of economical processes applicable to low-cost demineralization of sea and other saline water.

Except for minor editing, the data herein are as contained in a report submitted by the contractor. The data and conclusions given in the report are essentially those of the contractor and are not necessarily endorsed by the Department of the Interior.

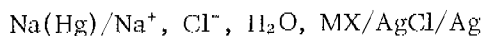
## I. INTRODUCTION

Desalination processes involve many different physical and chemical phenomena, but one common feature of nearly all their quantitative descriptions is the chemical potential of the saline components. Ideal laws, which give the dependence of chemical potential on solution composition in dilute solutions, tend to be poor approximations in the relatively concentrated solutions encountered in practice. The deviations of the actual chemical potentials from the ideal are usually expressed as activity coefficients which have been shown to be the relevant composition factors in processes involving reverse osmosis, electrodialysis, solvent extraction, adsorption, electrosorption, and scale formation. Thus, studies of activity coefficients in multicomponent saline solutions are of basic importance to the quantitative understanding and design of all desalination methods.

Since 1965, under OSW Contract No. 14-01-0001-607, we have been studying the activity coefficients of multicomponent salt solutions related to sea water. Details of the results and conclusions from this research have been presented in two interim reports<sup>1, 2</sup> and 13 papers published in scientific journals (see Section IX).

In this report, we shall briefly review the importance of activity coefficient data in desalination processes, and discuss the difficulty in making such data readily available for engineering application. Then we shall summarize the work done up till now on the present program, and show the need for further experimental work of the type we have been doing. Finally, we shall suggest additional experimental and theoretical work which we believe will contribute significantly to bridging the difficult gap between fundamental studies of solution thermodynamics and practical application of these results to realistic situations.

The principal experiments described in the First Interim Report were those which measured the activity of NaCl in multicomponent electrolytes using the cell:



for added salts (MX)  $\text{Na}_2\text{SO}_4$ , KCl, LiCl,  $\text{MgCl}_2$ , and  $\text{CaCl}_2$ . The conditions under which such a cell could be used were discussed.

The thermodynamics and kinetics of the alkali metal amalgam electrodes were discussed in detail, with emphasis on factors affecting the accuracy of measurements in cells such as the above. Interference by a second cation such as potassium or lithium was analyzed quantitatively. Measurements of the standard potential of the lithium amalgam electrode made during the course

of this research were reported.

The alkaline earth amalgam electrodes were also discussed, paying particular attention to the calcium and barium amalgam electrodes. Standard potentials were obtained for both these electrodes, using the best available thermodynamic data.

The experimental methods used in our research were discussed in detail. Techniques for handling amalgam electrodes, chloride-reversible and sulfate-reversible reference electrodes were described.

Results reported included activity coefficient measurements in the aqueous multicomponent systems  $\text{NaCl-Na}_2\text{SO}_4$ ,  $\text{NaCl-JiCl}$ ,  $\text{NaCl-CaCl}_2$ ,  $\text{NaCl-MgCl}_2$ , and  $\text{NaCl-BaCl}_2$ . Activity measurements using a calcium-selective liquid ion-exchange electrode were reported, and the theory of the activity of calcium ion in multicomponent solutions was discussed. A possible method based on the Brønsted theory for prediction of activity coefficients in multicomponent mixtures was presented. Experimental studies of the calcium and barium amalgam electrodes were summarized.

#### A. Relevance of Activity Coefficient Data

In our most recent interim report,<sup>2</sup> we gave a relatively detailed exposition of the role played by activity coefficients in the quantitative description of the desalination processes. Here, we will briefly review these ideas.

Distillation, for example, depends on the thermodynamic vapor pressure of the solution at the temperature of boiling, and hence on the activity of water in the multicomponent solution being distilled. It is possible to calculate the activity of water by knowing the activity coefficients of all the various saline components, using the Gibbs-Duhem relation. However, in practice, a fairly accurate approximation to the vapor pressure can be obtained simply from activity coefficient and heat of dilution data for  $\text{NaCl}$  solutions, with relatively simple ionic strength compensation for the presence of divalent ions.<sup>3,4</sup>

However, vapor pressure is not the only factor involved in the design and operation of a successful distillation plant, and other properties which are equally important cannot be predicted from such a simple model. Scale formation, for example, involves specific ionic equilibria which depend on the activity of minor components of the saline solution.<sup>5</sup> Corrosion and its inhibition depend on kinetics and equilibria involving the materials of construction, and may be critically dependent on relatively small changes in solution composition. Nucleation and growth of scale and pitting phenomena are also important, and these depend on chemical potential gradients in the boundary layer near the boiling surfaces. The use of saline water as a coolant for the condensers introduces still more corrosion problems, which again depend on chemical potentials and their gradients.

Next to distillation, the most important desalination processes are those dependent on solution transport through membranes: reverse osmosis and electrodialysis. All engineering design of such systems is ultimately based on transport equations which relate the flux of water and the various salt components to chemical potential gradients, electrical potential gradients,

and external hydrodynamic forces. In essentially all treatments of this class of problems, the chemical potential gradient has been expressed in terms of concentrations (making the approximation that all salt components are independent of each other and obey the ideal laws of dilute solutions). Of course, this is not the case, and the rigorous expansion of a chemical potential gradient,  $\nabla \mu_i$ , in a multicomponent solution includes cross terms for the dependence on the concentration of each component. Expressed in terms of activity coefficients, these are

$$\nabla \mu_i = v_i \nabla P + \sum_k (\partial \mu_i / \partial c_k) \nabla c_k \quad (1)$$

$$(\partial \mu_i / \partial c_i) = \frac{RT}{c_i} + \frac{RT}{\gamma_i} (\partial \gamma_i / \partial c_i) \quad (2)$$

$$(\partial \mu_i / \partial c_k) = \frac{RT}{\gamma_i} (\partial \gamma_i / \partial c_k), \quad i \neq k \quad (3)$$

In these expressions, the term  $RT/c_i$  is typically positive, of magnitude 0.5 to 5 kJ-ℓ/mol. The terms involving activity coefficients usually tend to become larger as the concentrations increase, and may reach magnitudes equal to that of the main term. In solutions of concentration near 1m, the activity coefficient terms are typically 10 to 20% of the main term. The cumulative effect of several such terms can thus exceed the magnitude of the term  $RT/c_i$ , but the activity coefficient terms are generally ignored at present in the analysis of membrane processes.

Thus, unless we have determined the activity coefficients of the various components in the multicomponent solutions we are dealing with, we may make errors of as much as 100% in analysis or prediction of the behavior of specific practical systems.

Another aspect of the membrane-based processes is the description and proper evaluation of the effects of a concentrated boundary layer formed near the membrane. In equations of hydrodynamic flow, which are based on the forces and fluxes outlined above, it is conventional to replace gradients of activity (which arise from chemical potential gradients) by gradients of concentration. The result is to introduce errors of the type discussed above. These show up as additional concentration dependence of parameters such as diffusion coefficients and ionic mobilities, thus limiting the usefulness of measurements made under particular circumstances for application to more general situations.

The activity of individual components is also of significance in other desalination processes. For example, the ultimate efficiency of a freezing process depends on the activity of water and salts in both the liquid phase and the solid phase, and only if there is a high degree of salt rejection from the solid phase can the process be effective. Solvent extraction processes depend on the activity of salt components both in the aqueous phase and the organic phase, and to predict the solubility of organic material in the aqueous phase, the effect of ionic components

on the activity of neutral molecules must be known. In adsorption processes, the essential factors are quite specific chemical and physical equilibria between the aqueous phase and the surface of the adsorbent, and again, these depend on the activity of ionic components in the aqueous phase. The use of total concentration instead of ionic activity makes the phenomena seem even more complicated than they really are. Electrosorption, in the same way, depends on the activity of dissolved species, and the structure of the electrical double layer at the electrode-solution interface involves chemical potential gradients and space charge layers of the same type as we discussed in connection with membrane processes.

Thus we can see that virtually all desalination processes involve the activity of ionic species, and the use of concentration as a substitute is often quite a poor approximation. Accurate knowledge of activity coefficients in multicomponent solutions would make it possible to describe these processes in terms of true chemical potentials and hence to avoid many errors of interpretation and extrapolation.

#### B. Obtaining Activity Coefficient Data

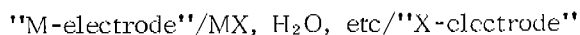
Any measurement which gives the chemical potential of one component of a solution can be used to obtain activity coefficients, but in practice, measurements on multicomponent solutions have generally been made either by electrochemical or isopiestic techniques. Other methods, such as freezing point, vapor pressure, osmotic pressure, solubility, ion exchange, and liquid-liquid extraction have been used less widely, and generally with less accuracy.

The isopiestic method is simple in concept. The experimental measurement consists of equilibrating the multicomponent solution through the vapor phase with a solution of known activity — usually a single solute for which the activity coefficients (or osmotic coefficients) have been obtained by electrochemical or direct vapor pressure measurement. The primary precautions required to obtain accurate results are: (1) to ensure exceedingly good thermal equilibration of the two solutions (this is usually done by using silver dishes resting on a silver block), and (2) to make very accurate weighings of the salts and equilibrated solutions to determine the concentrations accurately. Needless to say, the salts used must be very pure and their water content must be accurately known.

The isopiestic method is capable of high precision, but for solutions containing even two salt components, the evaluation of the activity coefficients of the solutes requires a complex mathematical analysis, and the accuracy of each final value depends to some extent on the accuracy of every measurement used in the analysis. For more than two salt components, ambiguities of this sort have thus far proven too formidable a challenge.

Electrochemical methods provide an ideal complement to the isopiestic measurements. Whereas the isopiestic experiment essentially measures the activity of water in the solution (with the activities of the salt components being obtained through thermodynamic relations), the electrochemical methods give the activity of a salt component directly. They thus provide an independent check on the validity of the thermodynamic relations used and on the accuracy of measurements by other methods.

The activity of a salt, MX, in a multicomponent solution may be measured directly if an electrode reversible to  $M^+$  (and affected by the concentration of no other ion in the solution) can be found, and if an electrode reversible to  $X^-$  (and affected by the concentration of no other ion in the solution) can be found. Then, the cell:



where

$m_M$  and  $m_X$  = the molal concentrations of the ions M and X

$\gamma$  = the mean activity coefficient of the salt MX in the multicomponent solution

$E^\circ$  = a standard potential obtained from measurements in solutions containing MX at known activity (or by extrapolation to infinite dilution)

$n$  = the number of electrons transferred (probably 1)

$R$  = the gas constant

$T$  = the absolute temperature

$F$  = the Faraday constant

has a potential given by:

$$E = E^\circ - \frac{RT}{nF} \ln [m_M m_X \gamma^2] \quad (4)$$

Examples of cation-reversible electrodes are the hydrogen electrode, metal amalgam electrodes, glass electrodes, and liquid ion-exchange electrodes. Examples of anion-reversible electrodes are silver-silver halide and lead amalgam-lead sulfate electrodes of the second kind, solid state membrane electrodes made of  $Ag_2S$  or  $LaF_3$ , and liquid ion-exchange electrodes. The most accurate electrochemical systems (e.g., hydrogen-silver chloride) give results reproducible to  $\pm 0.02$  mV, corresponding to an error of about 2 in the fourth decimal place of  $\log \gamma$ , or  $\pm 0.05\%$  in  $\gamma$ . Other systems are more susceptible to experimental errors, but even an accuracy of  $\pm 1$  mV will give  $\gamma$  to within  $\pm 2.5\%$ , which is a considerable improvement over the factor of 2 to 10 error resulting from the common approximation that all activity coefficients are unity.

### C. Presenting Activity Coefficient Data

How close are we to reaching the stage in which multicomponent activity coefficient data can be used with confidence in engineering design? For some simple situations, we have already at our disposal the required data, and the problem is largely one of making it available in a form which can be readily used. However, no comprehensive tables of activity coefficient data for solutions containing more than one salt component have yet been compiled, although some measurements are available on nearly a hundred systems, and bibliographic reviews have been

published.<sup>6, 7</sup>

The difficulty with making such data available for a usefully wide variety of systems is the lack of a simple and general theoretical framework in which to present experimental results. For relatively dilute aqueous solutions, there is no problem at all, since the Debye-Hückel theory and its simple extensions<sup>8, 9</sup> can provide an accurate estimation of activity coefficients in quite complex electrolyte mixtures, provided the total ionic strength is below 0.1m. If the ionic strength exceeds this limit, errors greater than 3% are encountered for univalent electrolytes, and at ionic strengths exceeding 1.0, the theoretical expressions lose all predictive value because of the complex and specific association phenomena between ions. This is precisely the range which is of most interest for desalination. The situation is even worse with polyvalent ions, since a whole series of stable ion pairs and coordination complexes may be present in the solution.<sup>9-11</sup>

Activity coefficients for electrolytes containing a single salt component have invariably been presented in tabular form for all concentrations higher than about 0.1m because of the difficulty of finding a simple algebraic form for the function. For the same reasons, accurate presentation of data for solutions containing two or more salt components becomes exponentially more cumbersome. The major components of sea water are the ions  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$ . These concentrations are restricted by the electroneutrality condition, so that there are only three independently variable components in a solution containing these four ions. If we include the temperature as an additional variable, and consider all accessible ranges of concentration, a compilation of activity coefficient data to cover in reasonable detail the solutions containing these four ions would require thousands of measurements. Of this hypothetical compilation, we can at present supply about 1% of the data, and some of this is not as accurate as we would like.

Although we know the activity coefficients of solutions containing each possible salt component (i.e.,  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{MgCl}_2$ ,  $\text{MgSO}_4$ ) alone in water, only for  $\text{NaCl}$  has a substantial temperature range been covered. Furthermore, we know the data for most solutions with two salt components only at 25 °C. Since some heat of mixing data is also available, this might be extended 10 to 20° in either direction without the loss of too much accuracy, but predictions for much higher temperatures could be quite uncertain. We have only scattered data on mixtures containing three salt components, mostly at compositions close to that of sea water. No systematic study has been made over a range of concentrations, and virtually no temperature dependence data are available at all.

If we now consider the other components present in sea water, brackish water, and various inland saline waters, the possible number of combinations becomes staggering. Additional species which are relevant include  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{H}^+$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{Br}^-$ ,  $\text{BO}_2^-$ ,  $\text{F}^-$ ,  $\text{OH}^-$ ,  $\text{H}_3\text{BO}_3$ , dissolved  $\text{CO}_2$ , dissolved  $\text{O}_2$ , as well as numerous trace metal ions and organic materials. Only an infinitesimal fraction of the required data is presently available.

Certainly, the immensity of this required body of data could be greatly reduced by means of adequate theories of ionic interactions. Even empirical relations which are orders of



magnitude more complex than the Debye-Hückel theory<sup>7</sup> are of help. But before further theories and empirical relations can be evolved and tested, we must have considerably more accurate and complete data than we do now.

#### D. Harned's Rule

At present, one important simplification that has been made in expressing data for multicomponent concentrations greater than 0.1m is the use of Harned's rule,<sup>6, 12, 13</sup> an approximate empirical relationship developed for solutions with two salt components:

$$\log \gamma_{12} = \log \gamma_{10} - \alpha_{12} X_2 I \quad (5)$$

where

$I$  = the ionic strength of the solution under consideration

$\gamma_{12}$  = the mean activity coefficient of salt 1 in the mixed electrolyte

$X_2$  = the ionic strength fraction of salt component 2

$\gamma_{10}$  = the mean activity coefficient of 1 in a solution containing only that salt, but at the same ionic strength  $I$

Thus, by using data obtained in a solution with only a single salt component ( $\gamma_{10}$ ) together with the composition of the solution with two salt components ( $I$  and  $X_2$ ), one can calculate  $\gamma_{12}$  from  $\alpha_{12}$  or vice versa.

The advantage of this formalism is that  $\alpha_{12}$  is a much less complicated function of composition. For most systems studied thus far, the Harned rule coefficient  $\alpha_{12}$  or  $\alpha_{21}$  has been found to be virtually independent of  $X_2$ , and in some cases (e.g., NaCl-Na<sub>2</sub>SO<sub>4</sub> or NaCl-KCl) nearly independent of  $I$  as well.<sup>7, 15, 16</sup> A comprehensive tabular presentation of  $\gamma_{12}$  would require about 800 numerical entries for each pair of salt components. Using Harned's rule, this table can be reduced (in these latter cases) to two numerical values ( $\alpha_{12}$  and  $\alpha_{21}$ ) with little loss in accuracy. Clearly, this is desirable if it can be done.

Still more desirable would be the possibility of calculating  $\gamma_{12}$  entirely from data for solutions containing each of the two components separately (i.e., from  $\gamma_{10}$  and  $\gamma_{20}$ ), but this has not proved sufficiently accurate. In some cases, however, a theory of this type (Brønsted-Guggenheim, for example) can provide a better estimate of  $\gamma_{12}$  than simply neglecting the specific interactions entirely ( $\alpha_{12} = \alpha_{21} = 0$ ).<sup>1, 6, 14</sup> The obvious extension of these ideas is the possibility of calculating activity coefficients in solutions containing three or more salt components from data obtained in simpler solutions. Thus far, not enough data have been collected to assess how accurately this can be done, although some progress has been made in correlating heats of mixing.<sup>17, 18</sup>

#### E. Chemical Models

One approach which may prove fruitful, particularly for solutions of many components,

is the "chemical model." Although it is well known that ionic interactions in relatively concentrated solutions do not obey the equations of simple chemical equilibria very accurately, it is possible, particularly in solutions where one salt component dominates, to describe approximately the effects of compositional variations on the activities of different components by a relatively simple model in which the strongest interactions are treated as ion-pairing equilibria. A significant application of this approach of natural water systems was the Garrels and Thompson chemical model for sea water<sup>19</sup> in which relatively crude approximations were made for calculating activity coefficients. Independent electrochemical measurements of the fraction of ionized magnesium<sup>20</sup> and calcium<sup>21</sup> have lent considerable support to the conclusions obtained from this model, and a recent critical reevaluation of these measurements<sup>22</sup> has resulted in even better agreement between calculated and measured values (Table I). It is particularly interesting to note that three completely independent experimental estimates of the percentage of free  $Mg^{2+}$  in sea water agree with the calculated value within  $\pm 1\%$ .

Table I. Percentage of Unassociated Cations in Sea Water at 25 °C, 1 Atm.

	Calculated <sup>19</sup>	Calculated <sup>22</sup>	Measured	Method
Free $Na^+$	99	$97.7 \pm 0.1$	$97.7 \pm 0.1$	Glass electrode <sup>22</sup>
Free $Mg^{2+}$	87	$89.0 \pm 0.3$	$88.1 \pm 0.3$	Liquid ion-exchange electrode <sup>22</sup>
			88	Liquid ion-exchange electrode <sup>20</sup>
			90	Ultrasonic absorption <sup>23</sup>
			90	Solubility of $Mg(OH)_2$ (brucite) <sup>24</sup>
Free $Ca^{2+}$	91	$88.5 \pm 0.5$	$86.3 \pm 0.9$	Liquid ion-exchange electrode <sup>22</sup>
			$82.0 \pm 2$	Liquid ion-exchange electrode <sup>21</sup>

Admittedly, sea water is a medium of relatively low ionic strength (0.67m) and consists primarily of NaCl, but there is no doubt that a chemical model can be of considerable predictive value in more concentrated solutions. For systems of relatively weak association, an ion-pairing model can give as good a fit to experimental measurements of activity coefficients as can Harned's rule. This has been verified for the multicomponent systems NaCl- $Na_2SO_4$ ,<sup>25</sup> NaCl- $NaHCO_3$ - $H_2O$ , and NaCl- $Na_2CO_3$ - $H_2O$ ,<sup>26</sup> and deserves further investigation in connection with more complex systems. An important aspect of this problem, which has not been fully clarified

yet, is the extent to which various nonthermodynamic assumptions involved in the chemical model affect the prediction of data which are important for desalination system design.

What does this mean for the designer of practical desalination systems? Certainly he will not wait until we have compiled libraries fully of activity coefficient data. But neither should he be forced to carry out his calculations with the meager amount of badly scattered data that we presently have available. If no theoretical framework for treating thermodynamic data for multicomponent systems is developed, then engineering design data must be measured under actual operating conditions, and optimizing the many variables involved becomes an enormously difficult task. Indeed, one may reasonably expect that libraries full of engineering data of less theoretical value, covering a considerably more restricted range of compositions, temperatures, and pressures, will eventually be accumulated.

We have tried to show here that for virtually all types of desalination process design it is desirable to have a large and varied body of activity coefficient data available. We have also tried to make it clear that only an extremely limited amount of such data has yet been measured, and that for even relatively simple systems it is quite essential to have a theoretical framework, no matter how primitive, to reduce the number of experiments and the amount of data tabulation to a manageable size.

## II. NaCl-NaHCO<sub>3</sub> AND NaCl-Na<sub>2</sub>CO<sub>3</sub> ELECTROLYTES\*

### A. Introduction

Despite the critical importance of bicarbonate and carbonate ions in natural water systems, little is known about the activity coefficients and ion-pairing equilibria of these species in the presence of alkali metal cations. Only one indirect study has been made<sup>2,7</sup> of the activity coefficients of NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> alone in aqueous solutions, but no direct measurements have been made of multicomponent activity coefficients, either of NaCl in the presence of carbonate species, or of carbonates in the presence of substantial concentrations of NaCl.

On the other hand, a large body of data has been collected on the protonation equilibria of carbonates,<sup>11,28,29</sup> mostly in media where extrapolation to infinite dilution is possible. Attempts<sup>29,30</sup> have been made to obtain quantitative information about ion-pairing equilibria from such data, but these rest on a number of ad-hoc assumptions regarding single ion activities and the constancy of liquid junction potentials, and for that reason are difficult to relate to thermodynamic data.<sup>2,31</sup>

Several experiments were designed to obtain the thermodynamic mean activity coefficient of NaCl in the presence of NaHCO<sub>3</sub> or Na<sub>2</sub>CO<sub>3</sub>, and the results were examined using an approach which includes not only the ion-pairing equilibria but also the effects of the protonation equilibria. In this way, we are approaching more closely the type of treatment which may give a useful chemical model for saline solutions of practical interest, and thus the approach is an instructive step in the development of such a chemical model.

The basic assumption for interpreting the mean activity coefficients of NaCl in the multicomponent electrolyte was described before.<sup>2</sup> This is that the observed mean activity coefficient,  $\gamma_{12}$ , for NaCl in the multicomponent electrolyte deviates from that observed in pure NaCl at the same ionic strength, because the concentration of free Na<sup>+</sup> has been depleted by the formation of ion pairs.<sup>31</sup> The model incorporates simultaneously the two previously postulated ion pairs NaHCO<sub>3</sub> and NaCO<sub>3</sub><sup>-</sup>, as well as the protonation equilibrium relating HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>.

We have left uncharged H<sub>2</sub>CO<sub>3</sub> and dissolved CO<sub>2</sub> out of this model because our measurements are made at pH values high enough that these acidic species are essentially

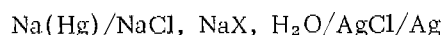
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\*Part of this work has been published in J. Phys. Chem., 74, 2976 (1970). Presented at the Symposium on Metal Ions in the Aqueous Environment, 158th National Meeting of the American Chemical Society (Division of Water, Air, and Waste Chemistry), New York, September 1969.

negligible. The difficulty with including  $\text{CO}_2$  is that one must then distinguish between an open system at constant partial pressure of  $\text{CO}_2$  and a closed system in which the total amount of  $\text{CO}_2$  in gas and solution phase is conserved. This distinction does not arise if only the ionic carbonate species are involved. In actual practice, one may encounter closed systems, open systems, or partially open systems in which the concentration of  $\text{CO}_2$  in solution is governed, e.g., by the rate of diffusion of  $\text{CO}_2$  away from the solution in the gas phase, and thus the equilibrium solution concentrations may be time-dependent because of these effects. Of course, such a more complete model would be of wider applicability of natural water systems, and could be developed.

## B. Experimental

Activity coefficients of NaCl were obtained as described previously from potential measurements of the cell:<sup>1, 32, 33</sup>



(where X represents  $\text{HCO}_3$  or  $1/2 \text{CO}_3^{2-}$ ), or from measurements of the cell:<sup>34</sup>



Two different types of sodium-selective glass electrodes were used. Electrode B was a Beckman no. 39278 sodium-ion electrode (glass composition<sup>35, 36</sup> LAS-10-23), and electrode C was a Corning no. 476210 sodium-ion electrode (glass composition NAS-11-18).

Solutions were prepared by weight from Fisher Certified reagent grade chemicals and triple-distilled water. NaCl contained less than 0.01% bromide, less than 0.002% iodide, and less than 0.0002% materials reducible by sodium amalgam.  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  contained less than 0.003% chloride, less than 0.01% bromide or iodide, and less than 0.0005% reducible metals. Solutions were analyzed for chloride by potentiometric titration with standard  $\text{AgNO}_3$ , for carbonate by potentiometric pH titration with standard  $\text{HCl}$ , and for bicarbonate by titration with standard  $\text{NaOH}$ . Gran<sup>37</sup> plots of these titration curves indicated negligible material other than chloride reacting with the silver ion, and less than 0.2% excess base in the carbonate.<sup>2, 31</sup> For the amalgam electrode measurements, 0.001M  $\text{NaOH}$  was added to the NaCl stock solution to minimize hydrogen evolution. The pH of each mixed solution was measured separately.

## C. Results

Representative potential measurements obtained with the amalgam electrode cell are given in Tables II and III. The values ( $\Delta E$ ) given are the difference in potential between a cell containing the mixed electrolyte and a cell containing the NaCl stock solution. The amalgam composition was the same, since both cells were fed from the same amalgam reservoir and were measured simultaneously. The Ag/AgCl electrodes were matched to better than  $\pm 0.01$  mV. Activity coefficients of NaCl in the mixed electrolyte ( $\gamma_{12}$ ) were calculated from the equation:

Table II. Activity Coefficient Measurements in NaCl-NaHCO<sub>3</sub>  
Electrolytes at 25 °C

[Cell: Ag/AgCl/NaCl, NaHCO<sub>3</sub>, H<sub>2</sub>O/Na(Hg)]\*

Total Ionic Strength I	X <sub>1</sub>	pH	ΔE, mV	-log γ <sub>12</sub> (Experimental)	-log γ <sub>12</sub> (Corrected) <sup>†</sup>
0.5031	1.0000	11.02	0	0.1672	0.1668
0.5073	0.7486	8.83	8.50 8.25	0.1791 0.1770	0.1784 0.1763
0.5133	0.5055	9.18	18.15 18.30	0.1782 0.1795	0.1767 0.1780
0.5215	0.1793	8.21	48.00 48.30	0.2092 0.2117	0.2064 ? 0.2089 ?
0.5240	0.0761	8.22	68.50 68.00	0.1974 0.1932	0.1941 0.1899
1.0981	1.0000	9.0	0	0.1838	0.1824
1.0400	0.4122	8.6	27.20 27.28	0.2102 0.2109	0.2087 0.2094
1.0115	0.1135	8.4	62.50 62.70	0.2225 0.2234	0.2219 0.2228
1.0049	0.0444	8.2	87.10 87.30	0.2255 0.2272	0.2252 0.2269

\*Component 1 is NaCl, component 2 is NaHCO<sub>3</sub>; I = m<sub>1</sub> + m<sub>2</sub>,  
X<sub>1</sub> = m<sub>1</sub>/I (protonation equilibria not included in calculating ionic strength);  
pH of 0.5m NaHCO<sub>3</sub> stock solution was 9.0; pH of 1.0m NaHCO<sub>3</sub> stock  
solution was 8.12.

<sup>†</sup>γ<sub>12</sub> corrected to round ionic strength (0.50 or 1.00) in last column.

Table III. Activity Coefficient Measurements in NaCl-Na<sub>2</sub>CO<sub>3</sub>  
Electrolytes at 25 °C

[Cell: Ag/AgCl/NaCl, Na<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>O/Na(Hg)]

Total Ionic Strength*	X <sub>1</sub>	pH <sup>†</sup>	ΔE, mV	-log γ <sub>12</sub> (Experimental)	-log γ <sub>12</sub> (Corrected)
0.5685	1.0000	8.3	0	0.1707	0.1669
0.5575	0.9096	10.24	3.57 3.70	0.1707 0.1718	0.1671 0.1682
0.5062	0.4868	10.89	26.98 26.65	0.1817 0.1789	0.1812 0.1784
0.4699	0.1880	11.07	56.50 56.10	0.1794 0.1761	0.1821 0.1788
0.4585	0.0944	10.99	77.30 76.97	0.1893 0.1865	0.1932 0.1904
1.0315	1.0000	9.04	0	0.1832	0.1824
1.0092	0.5069	10.1	25.50 25.40	0.2085 0.2076	0.2081 0.2072
0.9923	0.1357	10.8	66.10 65.80	0.2265 0.2240	0.2269 0.2244
0.9883	0.0483	10.9	94.28 93.95	0.2301 0.2273	0.2308 0.2280
3.0487	1.0000	10.90	0	0.1448	0.1465
3.0247	0.7459	10.98	14.70 14.00	0.1845 0.1786	0.1851 0.1792
2.9973	0.4831	11.15	31.80 31.71	0.2112 0.2104	0.2112 0.2104
2.9762	0.2621	11.00	54.40 54.30	0.2475 0.2466	0.2475 0.2466
2.9523	0.0532	11.35	100.92 100.65	0.2715 0.2692	0.2719 0.2696
1.0315 <sup>‡</sup>	1.0000	9.04	0	0.1832	—
1.9883 <sup>‡</sup>	0.5051	10.3	15.15 14.90	0.2441 0.2420	— —
2.6857 <sup>‡</sup>	0.1444	11.0	45.64 45.88	0.2764 0.2744	— —
2.8762 <sup>‡</sup>	0.0458	11.2	74.50 74.34	0.2797 0.2784	— —

\*I = m<sub>1</sub> + 3m<sub>2</sub>, X<sub>1</sub> = m<sub>1</sub>/I (protonation equilibria not included in calculating ionic strength).

<sup>†</sup>pH of 0.33m Na<sub>2</sub>CO<sub>3</sub> = 11.06; pH of 1.0m Na<sub>2</sub>CO<sub>3</sub> = 11.42.

<sup>‡</sup>These four solutions were at constant total molality rather than constant ionic strength.

$$E = E^{\circ} + \frac{RT}{F} \ln \left\{ m_{\text{Na}} m_{\text{Cl}} (\gamma_{12})^2 \right\} \quad (6)$$

with  $E^{\circ}$  evaluated from the known composition and activity coefficients of the NaCl stock solution.<sup>12</sup> Correction of  $\gamma_{12}$  to round ionic strength was made by assuming Harned's rule;<sup>13</sup>

$$\log \gamma_{12} = \log \gamma_{10} - \alpha_{12} I (1 - X_1) \quad (7)$$

where  $\gamma_{10}$  is the mean activity coefficient of NaCl alone at ionic strength  $I$ , and  $\alpha_{12}$  is estimated from the uncorrected data. A second iteration did not change the value of  $\alpha_{12}$  obtained from the corrected data.

Within experimental error, Harned's rule was obeyed for the amalgam electrode measurements in all solutions tested. Values of  $\alpha_{12}$  obtained by a least-squares fit to the corrected  $\gamma_{12}$  data in Tables II and III are given in Table IV. From all solutions tested at ionic strengths from 0.5 to 3.0, whether the second component was  $\text{NaHCO}_3$  or  $\text{Na}_2\text{CO}_3$ , the Harned rule coefficient fell in the range 0.045 to 0.050. This is an unexpectedly simple result.

Table IV. Harned Rule Coefficients

	$I$	pH	$\alpha_{12}$
NaCl- $\text{NaHCO}_3$	0.50	8.2 to 9.2	$0.050 \pm 0.009$
	1.00	8.2 to 8.6	$0.045 \pm 0.003$
NaCl- $\text{Na}_2\text{CO}_3$	0.50	10.2 to 11.1	$0.048 \pm 0.016$
	1.00	10.5 to 10.9	$0.049 \pm 0.003$
	3.00	10.9 to 11.4	$0.044 \pm 0.003$

Note:  $I$  is formal ionic strength, held constant for the series. For NaCl- $\text{NaHCO}_3$ ,  $I = m_1 + m_2$ ; for NaCl- $\text{Na}_2\text{CO}_3$ ,  $I = m_1 + 3 m_2$ . Effect of protonation equilibria on ionic strength not included. Errors on  $\alpha_{12}$  are 95% confidence limits obtained by the method of least squares, allowing the intercept to vary.

The glass electrode measurements in general confirmed the amalgam electrode results, but were less precise and apparently also less accurate. In particular, systematic deviations of the glass electrode measurements (Fig. 1) occurred at low fractions of NaCl in a direction which would imply that the activity of sodium ion in the vicinity of the glass surface was considerably enhanced over that in the bulk. (These deviations were not observed with the amalgam electrode cell.) The most pronounced deviations of this type were found in dilute NaCl- $\text{NaHCO}_3$  electrolytes; they were noticeable but less pronounced in NaCl- $\text{Na}_2\text{CO}_3$  electrolytes at low concentrations and were negligible at high concentrations (Fig. 2). Differences between glass electrodes B and C were noticeable, particularly in the dilute NaCl- $\text{NaHCO}_3$  electrolytes. Full data from these experiments are available.<sup>2, 31</sup>



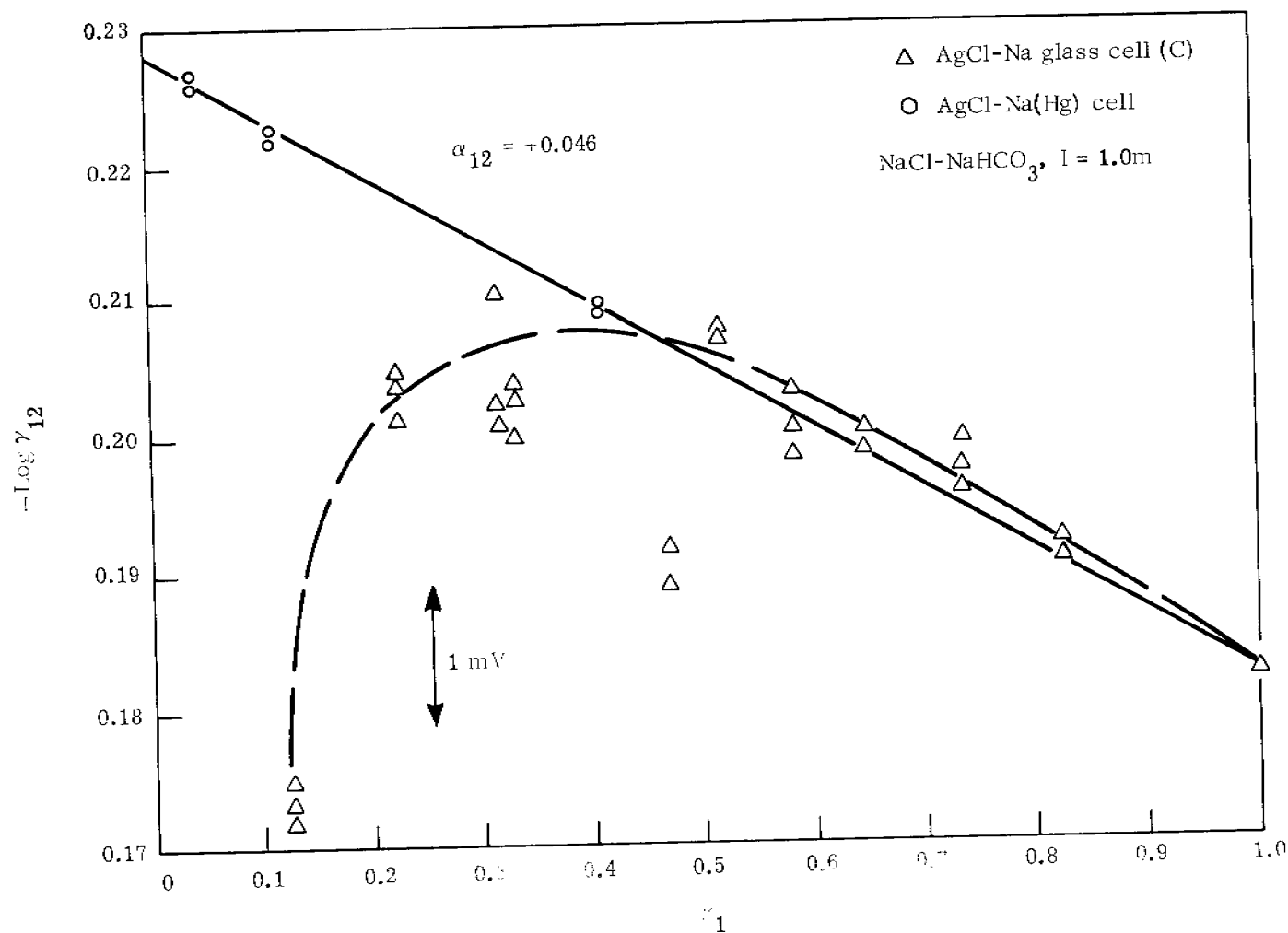


Fig. 1. Activity coefficients of NaCl in NaCl-NaHCO<sub>3</sub> electrolytes at ionic strength 1.0m (note deviations of glass electrode data)

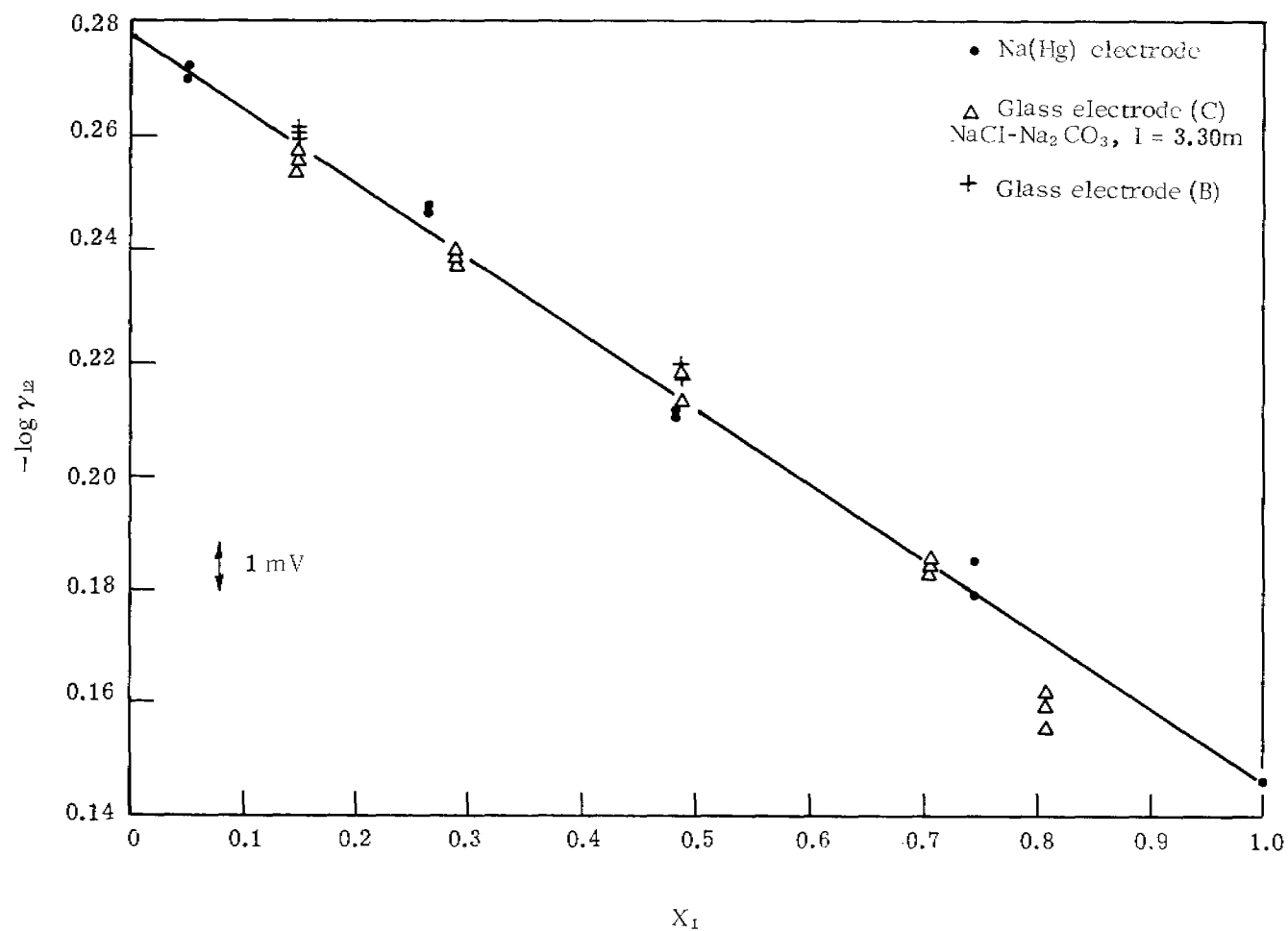


Fig. 2. Activity coefficients of NaCl in NaCl-Na<sub>2</sub>CO<sub>3</sub> electrolytes at ionic strength 3.0m

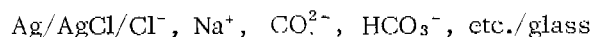
These differences appear to result from a specific but as yet unexplained effect on the glass electrode. Although the solutions used in the amalgam electrode experiments were somewhat more basic than those used in the glass electrode experiments (because of the addition of approximately 0.001M NaOH to the NaCl stock solution), the effect of this on ionic strength is negligible, corresponding to less than 0.002 mV error. The amalgam electrode experiments were also carried out in closed vessels using solutions saturated with hydrogen, but any concentration changes due to removal of carbon dioxide by the hydrogen were estimated to have a negligible effect (<0.05 mV) on the observed potentials.

Since the same set of Ag/AgCl electrodes was used for all experiments, this electrode cannot be the cause of the observed differences. No effect of hydrogen-saturated solutions compared to oxygen or carbon dioxide-saturated solutions is known to occur; in the presence of 1M chloride, formation of Ag<sub>2</sub>O requires pH values higher than 13 and formation of Ag<sub>2</sub>CO<sub>3</sub> is not expected to occur at all.<sup>11</sup>

Amalgam electrode dissolution in solutions of pH = 8.5 to 9 might have caused an excess concentration of Na<sup>+</sup> to build up in the vicinity of the electrode, and thus caused deviations from Harned's rule toward larger  $\gamma_{12}$  values at low NaCl fractions. Surprisingly, deviations in this direction were observed with the glass electrode but not with the amalgam electrode.

Thus, the deviations of the glass electrode measurements cannot be explained by any simple experimental effect. The deviations are apparently reproducible within 1 mV using different glass electrodes and making measurements at different times on different solutions, and may possibly be attributed to a specific adsorption of sodium ion on the glass surface which is somehow aided by the presence of bicarbonate ion in solution. Thus, the use of sodium-selective glass electrodes in carbonate-containing solutions should be tempered with some caution, since deviations of several millivolts from the thermodynamic values may be obtained.

We also carried out a few measurements of the protonation equilibria in NaCl media of ionic strength 1.0 and 3.0. In these experiments, we kept the NaCl concentration high compared to the total carbonate concentration, and used a cell without liquid junction. Since the solutions contain a fixed concentration of chloride already, the reference electrode was Ag/AgCl. The indicator electrode was a conventional glass pH electrode (Beckman 39301). The potential of the cell:



may be written in the form:

$$E = E^\circ + \frac{RT}{F} \ln \left\{ [H^+] [Cl^-] (\gamma_{21})^2 \right\} \quad (8)$$

where we have explicitly expressed the fact that  $\gamma_{21}$ , the mean activity coefficient of HCl in the medium (NaCl), is to be used.

These activity coefficient values in HCl-NaCl electrolytes have been measured by Harned and coworkers,<sup>38</sup> and may be represented by Harned's rule with the coefficient  $\alpha_{21}$ , = +0.0315 at  $I = 1$  and  $\alpha_{21} = +0.0300$  at  $I = 3$  (here component 1 is NaCl and component 2 is HCl). The mean activity coefficients of pure HCl ( $\gamma_{20}$ ) used to obtain  $\gamma_{21}$  from these coefficients ( $\alpha_{21}$ ) were obtained from the tables of Robinson and Stokes.<sup>12</sup> The results were  $\gamma_{21} = 0.7499$  at  $I = 1.054m$  and  $\gamma_{21} = 1.063$  at  $I = 3.098m$ . Using these values, together with the known chloride concentration ( $[Cl^-] = I$ ), we could relate  $E$  and  $[H^+]$  quantitatively.

The glass electrode was calibrated to obtain  $E^\circ$  by using a borax-NaCl buffer (0.01038m  $Na_2B_4O_7$  and 0.01925m NaCl) of ionic strength 0.030. It was known<sup>39</sup> to have:

$$p(a_H \gamma_{Cl}) = -\log \left( (\gamma_{21})^2 [H^+] \right) = 9.239 \text{ at } 25^\circ C \quad (9)$$

and  $[Cl^-] = 0.01925$ .  $E^\circ$  was calculated from Eq. (8).

In the titration of  $NaHCO_3$  with NaOH, the equation<sup>9</sup>

$$K_1 = \frac{1}{[H^+]} \left( \frac{1 - \phi}{\phi + K_{12} [H^+] (\phi + 1)} \right) \quad (10)$$

where

$$\phi = \frac{CV - (V + V_0) [OH^-]}{C_0 V_0}$$

and  $\log K_{12} = 6.0$  (ref. 40)

gives a value of  $K_1$  for each point. For the titration of  $Na_2CO_3$  with HCl, the equation:

$$K_1 = \frac{1}{[H^+]} \left( \frac{\phi}{1 - \phi + K_{12} (H^+) (2 - \phi)} \right) \quad (11)$$

where

$$\phi = \frac{CV + (V + V_0) [OH^-]}{C_0 V_0}$$

gives a value of  $K_1$  for each point. [The inclusion of  $K_{12}$  in Eq. (11) causes a change of  $< 0.005$  in  $\log K_1$  for  $pH > 8.5$ .] The computer programs for performing these calculations on sodium carbonate titrated with HCl (CARB2) and on sodium bicarbonate titrated with NaOH (BICARB3) are listed in Table V. The results of calculating the data from our three most accurate experiments are given in Table VI.

The variable PCT is the percent of the total titer value assumed to have been present in the initial sample. For example,  $PCT = 8$  in the titration of  $NaHCO_3$  with NaOH means that we have assumed that 8% of the  $NaHCO_3$  was converted to  $Na_2CO_3$  by loss of  $CO_2$ .  $PCT = 0$

# Table V. Computer Programs for Carbonate Titrations

12/16/69

>DUMP  
TO /CARR2/  
NEW FILE

>TYPE ALL

```
1.01 TYPE "TITRATION OF 25 ML NA2CO3(M2) IN M1 NACL WITH 1M HCL"
1.1 DEMAND DATA, PCT
1.12 OPEN DATA FOR INPUT AS FILE 1
1.15 READ FROM 1: M1, M2, G21, EB
1.16 VCOR = 25*M2*PCT/100
1.17 TYPE M1, M2, G21, EB
1.2 EO = EB + 647.9, L2 = 2* LOG10(G21)
1.22 TYPE EO
1.3 TYPE "
      V      E      CL      PH      LOG K1      I"
1.4 READ FROM 1: V,E
1.5 CL = (25*M1+V)/(25+V)
1.6 PH = (EO - E)/59.15 + LOG10(CL) + L2
1.61 V = V + VCOR
1.65 OH = 10^(PH-14)
1.66 PHI = (V + OH*(V+25))/(25*M2)
1.67 R = LOG10(PHI/(1-PHI)) IF PHI <1
1.68 R = -PH IF PHI >= 1
1.7 LK1 = R + PH
1.71 LK1 = 0 IF V<=0
1.75 IS = ((M1+3*M2)*25 - V)/(V+25)
1.8 TYPE IN FORM 1: V, E, CL, PH, LK1, IS
1.9 TO STEP 1.4
```

```
FORM 1:
      ????.??  ????.?  ???.????  ????.???  ????.???  ???.????
```

Table V (Cont.)

12/17/69

>LOAD

FROM /BICARB3/

>TYPE ALL

1.01 TYPE "TITRATION OF 25 ML  $\text{NaHCO}_3$  (M2) IN M1  $\text{NaCl}$  WITH 1M  $\text{NaOH}$ "

1.1 DEMAND DATA, PCT

1.12 OPEN DATA FOR INPUT AS FILE 1

1.15 READ FROM 1: M1, M2, G21, EB

1.16  $\text{VCOR} = 25 * \text{M2} * \text{PCT} / 100$

1.17 TYPE M1, M2, G21, EB

1.2  $\text{EO} = \text{EB} + 647.9$ ,  $\text{L2} = 2 * \text{LOG10}(\text{G21})$

1.22 TYPE EO

1.3 TYPE "

V E CL PH LOG K1 I"

1.4 READ FROM 1: V, E

1.5  $\text{CL} = (25 * \text{M1} + \text{V}) / (25 + \text{V})$

1.6  $\text{PH} = (\text{EO} - \text{E}) / 59.15 + \text{LOG10}(\text{CL}) + \text{L2}$

1.61  $\text{V} = \text{V} + \text{VCOR}$

1.65  $\text{OH} = 10^{(\text{PH} - 14)}$

1.66  $\text{PHI} = (\text{V} - \text{OH} * (\text{V} + 25)) / (25 * \text{M2})$

1.67  $\text{R} = \text{PH}$  IF  $\text{PHI} \leq 0$

1.675  $\text{R} = \text{PH}$  IF  $\text{PHI} > 1$

1.68  $\text{KH} = 10^{(6 - \text{PH})}$

1.69  $\text{R} = \text{LOG10}((\text{PHI} + \text{KH} * (\text{PHI} + 1)) / (1 - \text{PHI}))$

1.7  $\text{LK1} = \text{PH} - \text{R}$

1.71  $\text{LK1} = 0$  IF  $\text{V} \leq 0$

1.75  $\text{IS} = ((\text{M1} + \text{M2}) * 25 + 2 * \text{V}) / (\text{V} + 25)$

1.8 TYPE IN FORM 1: V, E, CL, PH, LK1, IS

1.9 TO STEP 1.4

FORM 1:

###.## #####.## ##.#### ##.### ##.### ##.####

Note:

G21 = mean activity coefficient of  $\text{HCl}$  in  $\text{NaCl}$  solution

EB = potential of cell in standard buffer solution (see Appendix)

V = titrant volume

E = potential after addition of V ml of titrant

Table VI. Results of Calculations on Carbonate Titrations

TITRATION OF 25 ML  $\text{NaHCO}_3(\text{M}_2)$  IN  $\text{M}_1$   $\text{NaCl}$  WITH  $1\text{M}$   $\text{NaOH}$   
 DATA = 'P71'

$\text{M}_1 = 1.0275000$   $\text{G}_21 = 0.74990000$   
 $\text{M}_2 = 2.6390700\text{E}-02$   $\text{EB} = -208$   
 $\text{EO} = 439.00000$

I	V	E	CL	PH	PCT = 0 PCT = 5 PCT = 8		
					LOG K1	LOG K1	LOG K1
1.0539	0.00	-88.5	1.0275	8.695	0.000	9.957	9.745
1.0543	0.01	-94.2	1.0275	8.791	10.566	9.938	9.763
1.0546	0.02	-98.0	1.0275	8.856	10.344	9.908	9.757
1.0550	0.03	-101.6	1.0275	8.916	10.230	9.889	9.756
1.0554	0.04	-104.7	1.0275	8.969	10.154	9.871	9.752
1.0558	0.05	-107.8	1.0274	9.021	10.104	9.861	9.753
1.0562	0.06	-110.5	1.0274	9.067	10.065	9.850	9.751
1.0569	0.08	-115.3	1.0274	9.148	10.008	9.832	9.746
1.0577	0.10	-119.4	1.0274	9.217	9.965	9.815	9.738
1.0584	0.12	-124.0	1.0274	9.295	9.948	9.816	9.746
1.0592	0.14	-127.5	1.0273	9.354	9.925	9.805	9.739
1.0599	0.16	-131.5	1.0273	9.422	9.918	9.807	9.746
1.0607	0.18	-134.2	1.0273	8.468	9.895	9.791	9.733
1.0614	0.20	-139.0	1.0273	9.549	9.912	9.814	9.758
1.0633	0.25	-148.4	1.0272	9.708	9.925	9.835	9.792
1.0651	0.30	-156.5	1.0272	9.844	9.928	9.841	9.789
1.0670	0.35	-164.4	1.0271	9.978	9.931	9.843	9.789
1.0688	0.40	-175.3	1.0271	10.162	9.985	9.892	9.833

TITRATION OF 25 ML  $\text{Na}_2\text{CO}_3(\text{M}_2)$  IN  $\text{M}_1$   $\text{NaCl}$  WITH  $1\text{M}$   $\text{HCl}$   
 DATA = 'P72'

$\text{M}_1 = 1.0127000$   $\text{G}_21 = 0.74990000$   
 $\text{M}_2 = 1.4080000\text{E}-02$   $\text{EB} = -211.10000$   
 $\text{EO} = 436.80000$

I	V	E	CL	PH	PCT = 0 PCT = 5 PCT = 10		
					LOG K1	LOG K1	LOG K1
1.0549	0.00	-207.0	1.0127	10.640	0.000	9.585	9.818
1.0541	0.01	-200.6	1.0127	10.531	9.276	9.590	9.737
1.0533	0.02	-195.0	1.0127	10.437	9.353	9.597	9.767
1.0525	0.03	-190.0	1.0127	10.352	9.404	9.603	9.754
1.0517	0.04	-185.8	1.0127	10.281	9.445	9.615	9.750
1.0508	0.05	-181.7	1.0127	10.212	9.471	9.620	9.743
1.0500	0.06	-178.0	1.0127	10.149	9.492	9.626	9.740
1.0492	0.07	-174.5	1.0127	10.090	9.509	9.631	9.738
1.0484	0.08	-171.0	1.0127	10.031	9.518	9.631	9.733
1.0476	0.09	-167.9	1.0127	9.979	9.530	9.636	9.733
1.0468	0.10	-164.8	1.0126	9.926	9.538	9.638	9.732
1.0459	0.11	-161.8	1.0126	9.875	9.544	9.640	9.732
1.0451	0.12	-158.8	1.0126	9.825	9.548	9.641	9.730
1.0443	0.13	-155.8	1.0126	9.774	9.550	9.640	9.728
1.0427	0.15	-150.4	1.0126	9.683	9.560	9.647	9.734
1.0411	0.17	-145.0	1.0126	9.591	9.567	9.654	9.742
1.0386	0.20	-136.5	1.0126	9.448	9.570	9.661	9.756
1.0370	0.22	-128.8	1.0126	9.318	9.542	9.638	9.742
1.0354	0.24	-122.3	1.0126	9.208	9.541	9.646	9.765
1.0338	0.26	-115.3	1.0126	9.089	9.542	9.663	9.808
1.0322	0.28	-105.4	1.0126	8.922	9.513	9.662	9.857
1.0306	0.30	-91.5	1.0125	8.687	9.449	9.654	9.990
1.0266	0.35	-20.4	1.0125	7.485	9.730	0.000	0.000

Table VI (Cont.)

TITRATION OF 25 ML  $\text{Na}_2\text{CO}_3(\text{M}_2)$  IN  $\text{M}_1$   $\text{NaCl}$  WITH  $1\text{M}$   $\text{HCl}$ .  
 DATA = 'P76'

$\text{M}_1 = 2.9558000$   $\text{G}_21 = 1.0630000$   
 $\text{M}_2 = 4.7450000\text{E}-02$   $\text{EB} = -204.50000$   
 $\text{EO} = 443.40000$

I	V	E	CL	PH	PCT = 0	PCT = 1	PCT = 3
					LOG K1	LOG K1	LOG K1
3.0981	0.00	-184.8	2.9558	11.144	0.000	9.757	9.945
3.0965	0.01	-177.9	2.9550	11.027	9.531	9.657	9.839
3.0949	0.02	-174.4	2.9542	10.968	9.546	9.656	9.821
3.0932	0.03	-170.5	2.9535	10.902	9.545	9.643	9.793
3.0916	0.04	-167.3	2.9527	10.848	9.556	9.642	9.779
3.0900	0.05	-164.4	2.9519	10.799	9.567	9.644	9.769
3.0883	0.06	-161.5	2.9511	10.750	9.573	9.642	9.758
3.0867	0.07	-158.7	2.9503	10.702	9.576	9.639	9.746
3.0851	0.08	-156.7	2.9496	10.668	9.591	9.649	9.748
3.0834	0.09	-153.8	2.9488	10.619	9.585	9.638	9.731
3.0818	0.10	-151.9	2.9480	10.587	9.595	9.644	9.732
3.0786	0.12	-148.0	2.9465	10.521	9.605	9.648	9.726
3.0753	0.14	-144.4	2.9449	10.460	9.611	9.650	9.720
3.0721	0.16	-141.0	2.9434	10.402	9.614	9.649	9.714
3.0689	0.18	-138.0	2.9418	10.351	9.619	9.651	9.711
3.0656	0.20	-135.1	2.9403	10.302	9.622	9.651	9.707
3.0576	0.25	-128.6	2.9364	10.191	9.626	9.652	9.700
3.0496	0.30	-122.2	2.9326	10.082	9.618	9.640	9.684
3.0416	0.35	-118.0	2.9288	10.011	9.637	9.658	9.698
3.0336	0.40	-112.4	2.9250	9.916	9.626	9.645	9.683
3.0257	0.45	-107.3	2.9212	9.829	9.618	9.636	9.672
3.0178	0.50	-103.0	2.9175	9.756	9.620	9.638	9.673
3.0099	0.55	-98.6	2.9137	9.681	9.619	9.637	9.671
3.0021	0.60	-94.4	2.9100	9.609	9.621	9.638	9.673
2.9943	0.65	-89.7	2.9062	9.529	9.614	9.631	9.667
2.9850	0.71	-84.6	2.9018	9.442	9.617	9.635	9.672
2.9788	0.75	-80.6	2.8989	9.374	9.610	9.629	9.668
2.9711	0.80	-75.3	2.8952	9.284	9.601	9.621	9.662
2.9634	0.85	-69.5	2.8915	9.185	9.589	9.610	9.655
2.9557	0.90	-63.2	2.8878	9.078	9.576	9.601	9.651
2.9481	0.95	-56.0	2.8842	8.956	9.561	9.589	9.648
2.9405	1.00	-48.5	2.8806	8.829	9.559	9.593	9.666
2.9330	1.05	-35.0	2.8770	8.680	9.487	9.532	9.633
2.9254	1.10	-17.0	2.8734	8.295	9.401	9.470	9.646
2.9179	1.15	12.8	2.8698	7.791	9.292	9.469	11.054

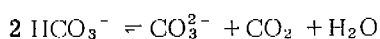


means that no excess acid or base is present.

In the titration of  $\text{NaHCO}_3$  with  $\text{NaOH}$ ,  $\text{PCT} = 0$  gives values of  $\log K_1$  which decrease systematically as the titration proceeds. In contrast,  $\text{PCT} = 8$  gives an almost constant value of  $\log K_1$ . In the titration of  $\text{Na}_2\text{CO}_3$  with  $\text{HCl}$  in 1M  $\text{NaCl}$ , the most constant value of  $\log K_1$  is obtained with  $\text{PCT}$  between 5 and 10, but the effect of changing  $\text{PCT}$  is more to shift the data as a group than to change the systematic trend, and an accurate estimate of  $\text{PCT}$  is not possible ( $\text{PCT} = 10$  gives good agreement with  $\text{NaHCO}_3$  titration). In the same titration in 3M  $\text{NaCl}$ , a much better fit is obtained; this time with  $\text{PCT} = 1$ , indicating that the  $\text{Na}_2\text{CO}_3$  as initially prepared probably contained less than 1% of free acid or base. We believe that in the solutions used in the 1M  $\text{NaCl}$  titrations the  $\text{NaHCO}_3$  lost about 0.002M  $\text{CO}_2$  to the atmosphere and the  $\text{Na}_2\text{CO}_3$  gained about 0.001M  $\text{CO}_2$ . The results of these calculations are summarized in Table VII. Some values of  $K_1$  at lower ionic strengths, calculated from the pH of standard buffers,<sup>13</sup> are also included.

## 10. DISCUSSION

The first question to be considered is what effect the carbonate protonation equilibria may have on the measured values of activity coefficient for  $\text{NaCl}$  in the presence of carbonate or bicarbonate. Shifts in these equilibria under the conditions of our experiments could result from loss or gain of  $\text{CO}_2$ . This would not affect the concentrations of either  $\text{Na}^+$  and  $\text{Cl}^-$ , but the total ionic strength would be affected because of the transformation of two singly-charged ions into a doubly-charged ion (or the reverse):



Loss of  $\Delta m$  mol/kg of  $\text{CO}_2$  would increase the ionic strength of the solution by an amount  $\Delta m$ . Our observations on the relatively dilute carbonate and bicarbonate solutions used to determine  $K_1$  indicated that during the normal course of laboratory manipulations, without taking special precautions to seal the solution against the atmosphere,  $\text{NaHCO}_3$  solutions lost about 0.001m  $\text{CO}_2$  and  $\text{Na}_2\text{CO}_3$  solutions gained about 0.001m  $\text{CO}_2$ . The partial pressure of  $\text{CO}_2$  above a bicarbonate solution with pH = 8.5 is approximately 1 torr, and that above a carbonate solution with pH = 10.5 is approximately 0.001 torr.<sup>11</sup> This gain and loss is thus reasonable when one considers that the normal partial pressure of atmospheric  $\text{CO}_2$  falls well within this range.

What would then be the expected magnitude of the effect of  $\text{CO}_2$  gain or loss on  $\gamma_{12}$  for  $\text{NaCl}$  in the mixed electrolytes we have been studying? At ionic strengths near 1.0, a change of 0.1m in ionic strength produces a change of about 0.001 in  $\log \gamma_{12}$ , corresponding to less than 0.1 mV in the measured cell potential. At ionic strengths near 3.0, a shift in  $I$  of 0.1m produces a change in  $\log \gamma_{12}$  corresponding to about 0.3 mV. The expected exchange of  $\text{CO}_2$  with the vapor phase is considerably less than 0.1m, and thus these effects are made smaller than the experimental errors, and have an entirely negligible effect on the measured activity coefficients.

Table VII. Acid-Base Equilibrium of Carbonate in NaCl

Ionic Strength*	Initial Solution		Titrant	Log $K_1$ †	
	NaHCO <sub>3</sub> , m	Na <sub>2</sub> CO <sub>3</sub> , m			
1.056 — 1.069	0.0243	0.0031	1.00M NaOH	9.75 ± 0.05	
1.055 — 1.031	0.0010	0.0130	1.00M HCl	9.68 ± 0.10	
3.098 — 2.925	0.0005	0.0470	1.00M HCl	9.63 ± 0.03	
Estimate from pH of Standard Buffers ‡					
			pH	-log $\gamma_H$	
0.04	0.01	0.01	10.112	0.074	10.038
0.10	0.025	0.025	10.018	0.099	9.918
0.20	0.05	0.05	9.933	0.115	9.817

\*Primarily NaCl. A change of about 3% occurs during titration because of dilution and shifts in equilibria. The values given are the initial and final ionic strengths calculated in the course of determining  $K_1$ .

† Equilibrium constant for the reaction  $H^+ + CO_3^{2-} = HCO_3^-$  (IUPAC notation). Standard state, unit molality to NaCl of ionic strength 1.06 or 3.00. Neglecting the minor component of the initial solution caused errors of about 0.2 logarithmic unit in  $K_1$  for the first two titrations.

‡ Data from Ref. (13), pp 712 and 716,  $\log K_1 = \text{pH} + \log \gamma_H + \log (1 - K_1 K_{12} [H^+]^2) - \log 1 + 2K_{12} [H^+]$ .  $\gamma_H$  was assumed equal to  $\gamma_{\pm}$  for HCl.

The second question to be considered is a possible explanation of the relatively large and highly consistent values of the Harned rule coefficient,  $\alpha_{12}$ , which were obtained in our experiments. The addition of carbonate or bicarbonate to NaCl at constant ionic strength decreases the activity of NaCl by an amount corresponding to as much as 10 mV in potential; and a natural explanation may be sought in a model where ion pairs such as  $\text{NaHCO}_3$  and  $\text{NaCO}_3^-$  are formed. A simple criterion for the self-consistency of such a model is whether the formation constants of these complexes are relatively independent of composition at constant ionic strength, and whether the variation of the formation constants with ionic strength is consistent with expectations based on charge type. A final criterion lies in the agreement of calculations based on formation constants obtained from activity coefficient measurements, with observations of the effect of different ionic media on the carbonate protonation equilibria.

Previous estimates of ion-pairing equilibrium constants<sup>19, 30</sup> have depended on rather uncertain values of activity coefficients for alkali carbonates and bicarbonates,<sup>2, 7</sup> pH measurements in cells with liquid junction, and nonthermodynamic assumptions for single ion activity coefficients.<sup>4, 1</sup> In our analysis, we have attempted to be as explicit as possible about any non-thermodynamic assumptions introduced. We have been guided in our analysis by the discussion of the NaCl- $\text{Na}_2\text{SO}_4$  system in a recent paper by Pytkowicz and Kester,<sup>2, 5</sup> who showed that for weak association between  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  a relationship approximating Harned's rule (with positive  $\alpha_{12}$ ) was obtained from a simple ion-pairing model.

For the NaCl (component 1)- $\text{Na}_2\text{CO}_3$  (component 2)- $\text{NaHCO}_3$  (component 3) system, we have made the following assumptions:

1. The species present in the solution in appreciable concentrations were  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{NaCO}_3^-$ , and  $\text{NaHCO}_3$  (a neutral ion pair).
2. The mean activity of NaCl changes only as a result of ion-pair formation, provided the total ionic strength is held constant. This may be expressed as:

$$[\text{Na}^+][\text{Cl}^-]\gamma_{\text{Na}}\gamma_{\text{Cl}} = (m_1 + 2m_2 + m_3)m_1(\gamma_{12})^2 \quad (12)$$

where  $(m_1 + m_3)$  is the total concentration of sodium ion and  $[\text{Na}^+]$  is the equilibrium concentration of free sodium ion. Since no ion pairs are formed by chloride,  $[\text{Cl}^-] = m_1$ , and we may define the mean activity of free  $\text{Na}^+$  and  $\text{Cl}^-$  ions to be  $\gamma_1 = (\gamma_{\text{Na}}\gamma_{\text{Cl}})^{1/2}$ :

$$[\text{Na}^+](\gamma_1')^2 = (m_1 + 2m_2 + m_3)(\gamma_{12})^2 \quad (13)$$

Thus  $\gamma_1'$  is assumed to be equal to the mean activity coefficient of NaCl at ionic strength  $I'$ . This ionic strength is calculated not on a formal basis but on the basis of the equilibrium concentrations of the various ionic species:

$$I' = 1/2 \{ [\text{Na}^+] + [\text{Cl}^-] + [\text{HCO}_3^-] + 4[\text{CO}_3^{2-}] + [\text{NaCO}_3^-] \} \quad (14)$$

These equilibrium concentrations, in turn, are obtained from the ion pairing and protonation equilibria:

$$[\text{HCO}_3^-] = K_1 [\text{H}^+] [\text{CO}_3^{2-}] \quad (15)$$

$$[\text{NaCO}_3^-] = K_1' [\text{Na}^+] [\text{CO}_3^{2-}] \quad (16)$$

$$[\text{NaHCO}_3] = K_1'' [\text{Na}^+] [\text{HCO}_3^-] \quad (17)$$

together with the mass balances on the three components:

$$[\text{Cl}^-] = m_1 \quad (18)$$

$$[\text{Na}^+] + [\text{NaHCO}_3] + [\text{NaCO}_3^-] = m_1 + 2m_2 + m_3 \quad (19)$$

$$[\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{NaHCO}_3] + [\text{NaCO}_3^-] = m_2 + m_3 \quad (20)$$

An iterative procedure was used to obtain the best values for the ion-pairing constants at each ionic strength.  $K_1$  was taken from Table IV ( $\log K_1 = 9.63$  at  $I = 3$ ,  $9.75$  at  $I = 1$ ,  $9.8$  at  $I = 0.5$ ). For the first iteration, we assumed  $\log K_1' = +0.5$  and  $\log K_1'' = -0.5$ , values obtained in a less rigorous treatment.<sup>2, 31</sup>

From each experimental value of  $\gamma_{12}$ , a refined value of  $K_1'$  ( $\text{NaCl-Na}_2\text{CO}_3$  electrolytes) or  $K_1''$  ( $\text{NaCl-NaHCO}_3$  electrolytes) was obtained by the following procedure. Assuming  $I' = I$ ,  $\gamma_1$  was obtained from data for pure  $\text{NaCl}$  solutions, and using the experimental  $\gamma_{12}$   $[\text{Na}^+]$  was calculated by Eq. (13). The remainder of the concentrations were calculated using Eqs. (15) to (20), and a revised value of  $I'$  was calculated from Eq. (14). This procedure was repeated until two successive values of  $I'$  agreed to within  $0.0001$ , at which point either  $K_1'$  or  $K_1''$  was calculated from Eq. (16) or Eq. (17). The computer programs and details of the numerical results are given in full elsewhere.<sup>2, 31</sup>

The average values of  $K_1'$  and  $K_1''$  obtained at each ionic strength were then used as starting values for second and third approximations by the above procedure. The fourth approximation gave values of the constants which differed by less than  $0.001$  logarithmic units, and these are given in Table VIII, together with their statistical 95% confidence limits.

The curve of  $\log \gamma_{12}$  versus  $X_1$  calculated from these constants is nearly straight, even in the case where ion pairing is strongest:  $\text{NaCl-Na}_2\text{CO}_3$  at  $I = 3$ . In Fig. 3, the comparison is made with Harned's rule, which seems to be a slightly better fit to the experimental data. An additional curve, calculated assuming  $I' = I$ , shows what a large effect the formation of ion pairs has on the ionic strength of the medium. Although the ion-pairing model seems to give a slightly poorer fit than Harned's rule, it has the advantage of being easily extended to systems of many components, in a "chemical model." Such models are often invoked, and the approach described here provides a self-consistent and minimal set of empirical assumptions.

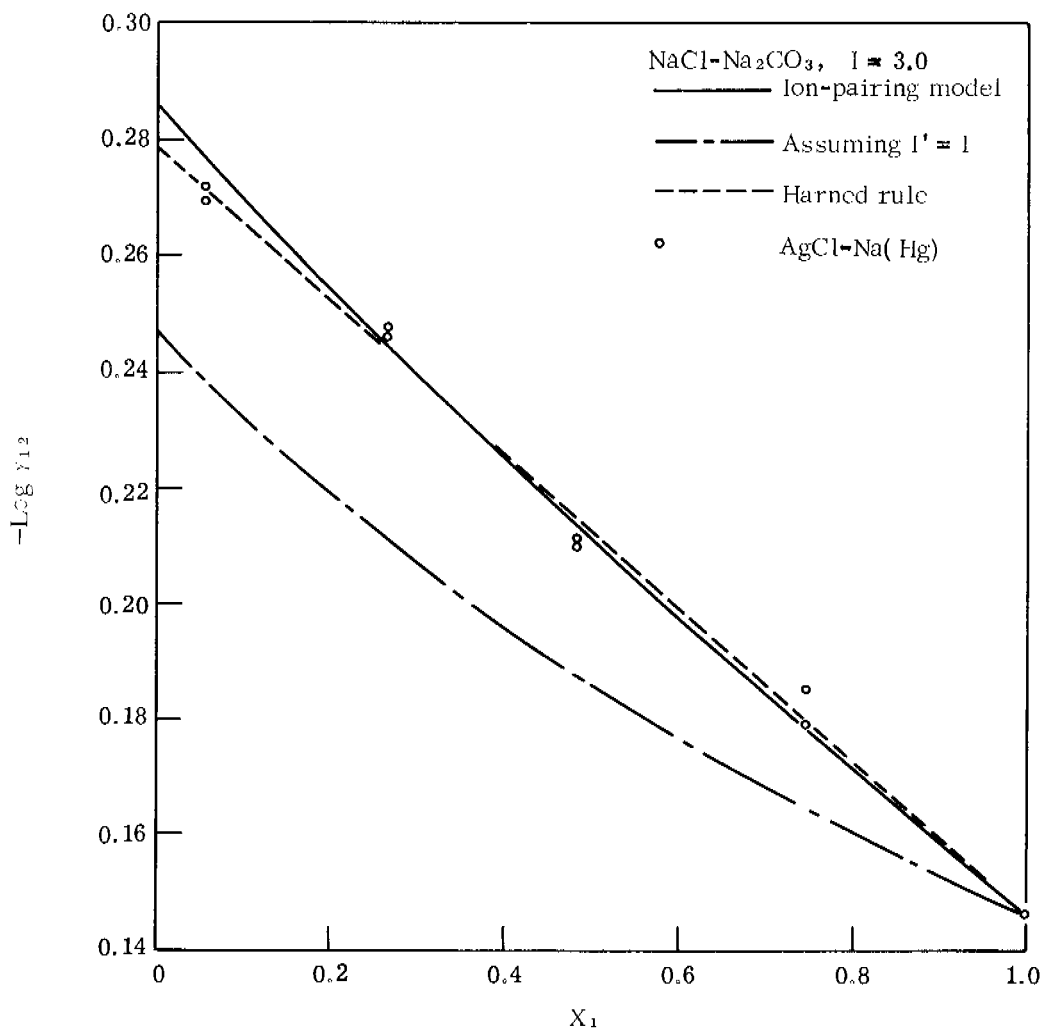


Fig. 3. Application of the ion-pairing model to NaCl-Na<sub>2</sub>CO<sub>3</sub> electrolytes at ionic strength 3.0 m. Parameters used in calculations:  $\alpha_{12} = 0.044$  for Harned's rule;  $\log K'_1 = +0.37$ ,  $\log K''_1 = -0.67$ ,  $\log K_1 = 9.63$ , pH = 11.2 for the ion-pairing model

Table VIII. Ion-Pairing Constants\*

Ionic Strength or Reference	log $K_1'$		log $K_1''$	
	Measured	Corr to $I = 0$	Measured	Corr to $I = 0$
3.0	$+0.37 \pm 0.06$	$+0.97 \pm 0.23$	—	—
1.0	$+0.27 \pm 0.07$	$+0.96 \pm 0.13$	$-0.67 \pm 0.10$	$-0.30 \pm 0.13$
0.5	$+0.14 \pm 0.16$	$+0.77 \pm 0.18$	$-0.41 \pm 0.19$	$-0.08 \pm 0.20$
Ref. 30		+1.27		-0.26
Ref. 29 ( $<0.01$ )		+0.55		$+0.16 \pm 0.06$

\* $K_1'$  is the formation constant for  $\text{NaCO}_3^-$  and  $K_1''$  is the formation constant for  $\text{NaHCO}_3$  at the ionic strengths given. Errors on the measured values are 95% confidence limits based on the mean square deviation of values corresponding to each experimental point in Tables II and III. Corrections to  $I = 0$  were made with estimated activity coefficients<sup>2, 31</sup> and the confidence limits have been increased to reflect the estimated error in these values.

Note that the ion-pairing model does not explain the deviations (Fig. 1) to smaller values of  $-\log \gamma_{12}$  at low values of  $X_1$ . For  $\text{NaCl-NaHCO}_3$  electrolytes, the calculated curves are almost straight and give about as good a fit to the data as does Harned's rule. Although pH has little effect (in the range near 11.0) on the  $\text{NaCl-Na}_2\text{CO}_3$  calculations, it has a much stronger effect on the  $\text{NaCl-NaHCO}_3$  calculations. At pH 8.2 to 8.6, approximately 2 to 10% of  $\text{HCO}_3^-$  is present as  $\text{CO}_3^{2-}$ , and since the ion pairs of  $\text{Na}^+$  with  $\text{CO}_3^{2-}$  are an order of magnitude stronger than those with  $\text{HCO}_3^-$ , a relatively small change in pH can cause a relatively large change in  $[\text{Na}^+]$  and hence in  $\gamma_{12}$ .

The first test of self-consistency (i.e., that the constants be independent of composition at constant ionic strength) is satisfied quite well for this system. The second test (i.e., that the variation of the constants with ionic strength be consistent with the charge type of the ions involved) may be examined only very approximately at these high ionic strengths, since no rigorous theory exists by which the dependence of these particular combinations of activity coefficients on ionic strength may be determined apart from the experiments we have just performed.

Examination of various approximations for activity coefficients (e.g.,  $\gamma_{\pm}$  for  $\text{NaCl}$  values for the carbonate and bicarbonate ions calculated by Walker, et. al.,<sup>27</sup> and the MacInnes assumption  $\gamma_K = \gamma_{\text{Cl}}$  employed by Garrels<sup>19, 30</sup>) led us to estimates for the ion-pairing constants at  $I = 0$  reported in Table VIII. Details are given elsewhere.<sup>31</sup>

As we have mentioned above, further evidence for ion-pairing between  $\text{Na}^+$  and  $\text{CO}_3^{2-}$  or  $\text{HCO}_3^-$  may be obtained from the variation of the acid-base equilibrium constants with ionic strength. Some representative values (refs. 42 through 47) are plotted along with data from Table VII in Fig. 4. The ionic medium and reference is noted next to each point. Qualitatively, the association constant of  $\text{HCO}_3^-$  or  $\text{CO}_3^{2-}$  with  $\text{H}^+$  ( $K_{12}$  or  $K_1$ ) decreases in the presence of

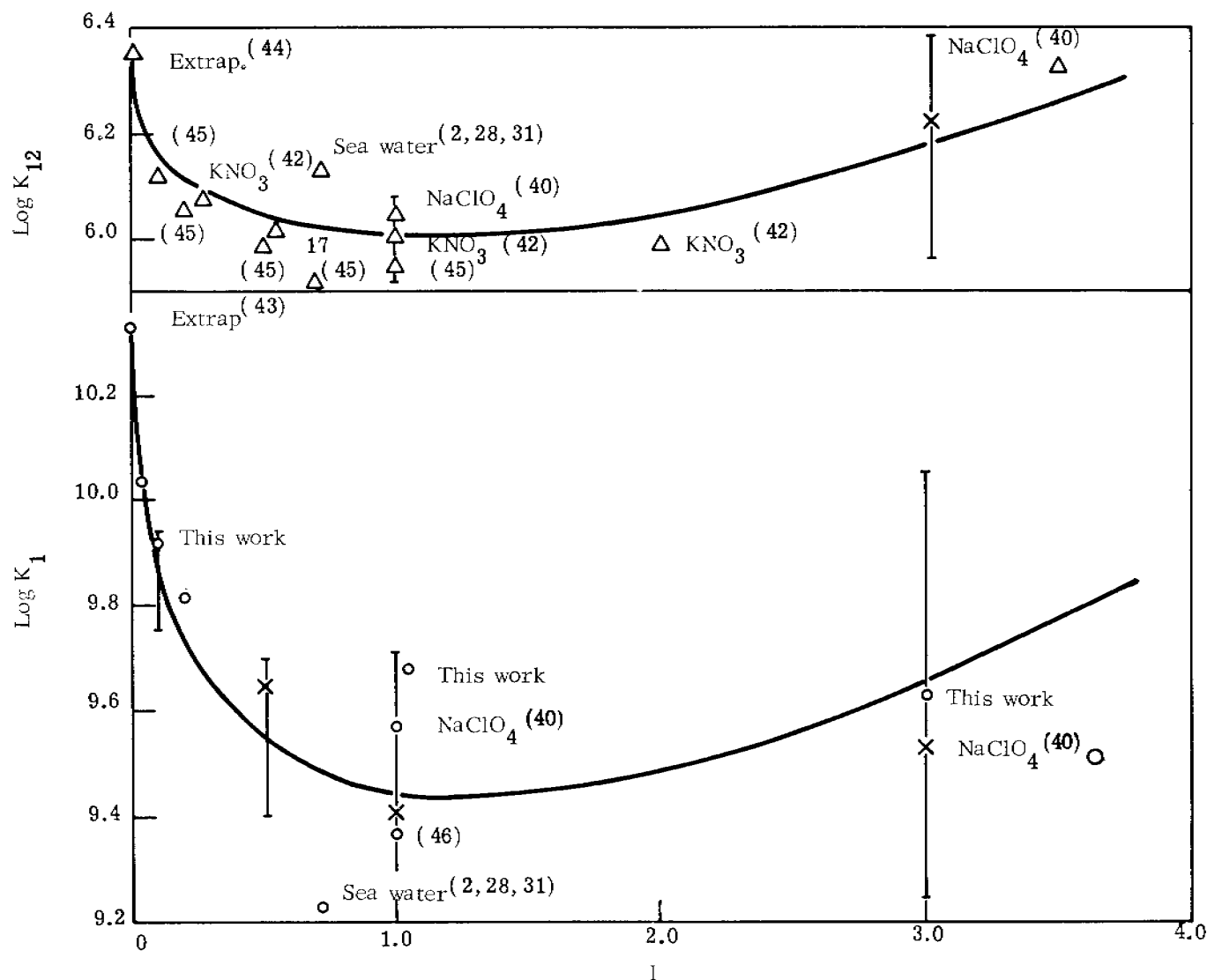


Fig. 4. Ionic strength effect on protonation equilibrium constants. The medium is NaCl unless otherwise specified, and references are given in parenthesis. Curves were calculated from estimated activity coefficients<sup>2,31</sup> and the ion-pairing constants of Table VIII

added salt in the direction predicted by assuming that the cation of the added salts is competing with  $H^+$  for the carbonate ligand. The differences are small for  $K_{12}$ , but much larger for  $K_1$ .

However, the effect of increased ionic strength on the activity coefficients also causes the concentration equilibrium constants  $K_1$  and  $K_{12}$  to shift in the observed direction. Separation of these two effects may be made by one of two alternatives: (1) either the ion-pairing effect is known from other experiments, or (2) the activity coefficient effect is known from other experiments. Both involve nonthermodynamic assumptions. Most workers<sup>28-30</sup> have calculated activity coefficients of the species involved and have obtained estimates of ion pairing from the ionic strength effect on the protonation equilibria. We have approached from the other direction and have obtained an estimate of the ion-pairing effect from an independent set of experiments.

If the ionic medium (e.g., NaCl) is present in large excess,  $[Na^+]$  is determined only by the total ionic strength and is essentially fixed. Since  $[NaCO_3^-]$  and  $[CO_3^{2-}]$ , or  $[NaHCO_3]$  and  $[HCO_3^-]$  are indistinguishable by the usual pH methods, and are measured in toto, we have

$$\left( [HCO_3^-] + [NaHCO_3] \right) = K_1 [H^+] \left( [CO_3^{2-}] + [NaCO_3^-] \right) \quad (21)$$

and hence

$$K_1 = K_1^\circ \left( \frac{\gamma_H \gamma_{CO_3}}{\gamma_{HCO_3}} \right) \left( \frac{1 + K_1^\parallel [Na^+]}{1 + K_1^\parallel [Na^+]} \right) \quad (22)$$

where  $K_1^\circ$  is the acid-base equilibrium constant at zero ionic strength and the activity coefficients are hypothetical single-ion values for which only electrically neutral combinations (e.g.,  $\gamma_{Na}$  and  $\gamma_{HCO_3}$ ) can be empirically determined.  $K_1^\parallel$  and  $K_1^\parallel$  are formation constants determined in the medium of interest, such as we have given in Table VIII.

Similarly, we obtain:

$$K_{12} = K_{12}^\circ \left( \frac{\gamma_H \gamma_{HCO_3}}{\gamma_{CO_2}} \right) \left( \frac{1}{1 + K_1^\parallel [Na^+]} \right) \quad (23)$$

The curves drawn on Fig. 4 were obtained by means of these equations using the accepted<sup>43,44</sup> values for the zero-ionic strength constants, the previously estimated activity coefficients,<sup>31</sup> and the ion-pairing constants of Table VIII. The vertical bars indicated their estimated uncertainty. The contribution of ion pairing to the change in log K is approximately half that of the activity coefficient term for both  $K_1$  and  $K_{12}$  over the whole ionic strength range, with the exception of  $K_{12}$  at  $I = 3$ , where ion pairing is the principal contribution. The agreement with experimental values is excellent for  $K_{12}$  and certainly within the expected uncertainty for  $K_1$ .

It appears that there is little specific effect of chloride since NaCl and NaClO<sub>4</sub> media give comparable values for both constants. Similarly, although  $K^+$  has been assumed to give



weaker ion pairs than  $\text{Na}^+$  with the carbonate species,<sup>30</sup> this must be compensated for by association between  $\text{H}^+$  and  $\text{NO}_3^-$ , since  $\text{KNO}_3$  gives the same values for  $K_{12}$  as does  $\text{NaClO}_4$  or  $\text{NaCl}$ . Sea water gives a considerably smaller value for  $K_1$ , which can be reasonably attributed to the formation of magnesium carbonate ion pairs,<sup>11, 19, 28, 30</sup> and the fact that there is little difference between  $K_{12}$  in sea water and  $\text{NaCl}$  indicates in turn that magnesium-bicarbonate ion pairs are rather weak. Perhaps the most important gap in the present collection of data is a reliable set of experimental values for  $K_1$  in  $\text{NaCl}$  over a wide range of ionic strength. Our experiments at  $I = 1.0$  (Table VII) did not agree with the spectrophotometric data obtained by Bruckenstein and Nelson,<sup>4, 6</sup> and although values of  $K_1$  higher than the curve are suggested by the low ionic strength data, the  $\text{NaClO}_4$  results<sup>40</sup> are lower than ours. One possible explanation could lie in a specific effect of carbonate on the species of the thymol blue indicator used but this has not been investigated further.

As a final point, we should note that the ion-pairing constants of other workers<sup>29, 30</sup> quoted in Table VIII were in essence obtained from the ionic strength effect on the protonation equilibria. The value of the ion-pairing constants obtained from such an analysis is critically dependent on the assumptions used to calculate the activity coefficients of the ions. As we have seen, the activity coefficient contribution to the ionic strength effect is about twice as large as the ion-pairing effect. In particular, the activity coefficient term in  $K_1$  involves  $\gamma_{\text{CO}_3^{2-}}$ , and this is the major contribution to the uncertainty in values of  $K_1$  calculated from the ionic strength dependence of  $K_1$ . Garrels and co-workers<sup>19, 30</sup> obtained  $\gamma_{\text{CO}_3^{2-}}$  from the paper by Walker, et al.,<sup>27</sup> and Nakayama<sup>29</sup> estimated it from the extended Debye-Huckel equation. These two sets of values may in fact represent the extremes of the range which can be obtained with different activity coefficient assumptions. Our values fall well within this range, and thus our model is as consistent as can be expected with previous estimates of ion-pairing between  $\text{Na}^+$  and  $\text{HCO}_3^-$  or  $\text{CO}_3^{2-}$ . It has the advantage of requiring a minimum of ad-hoc assumptions.

## APPENDIX TO SECTION II

For experiments done either with NaCl-NaHCO<sub>3</sub> solutions or with NaCl-Na<sub>2</sub>CO<sub>3</sub> solutions, calculations were set up to deal with one or the other of these two-salt-component situations in the same sequence of calculations which we had previously used for the simpler model (in which only one possible equilibrium was dealt with instead of three). The computer program used for these calculations is given in Table IX. This table incorporates all the features of the programs /PYT/ and /PYT2/ which were given in the Second Interim Report.<sup>2</sup> In addition, we have made use of the more complete mass balance equations given below. Part 1 sets executive parameters (SAL, AUT, INP) which govern the flow of program in other parts. Decisions are made as to: (1) which salt (carbonate or bicarbonate) is added to NaCl, (2) whether individual points are to be calculated or whether a curve is to be calculated in automatically prescribed steps, and (3) what sort of input is going to be provided (equilibrium constant, Harned rule coefficient, or log  $\gamma_{12}$ ).

Part 3 calculates the appropriate ion-pairing constant KS (K<sub>1</sub> if SAL = CAR, K<sub>1</sub>' if SAL = BIC), given a Harned rule coefficient or a mean activity coefficient for NaCl (in the latter case, entry is through part 5). The algorithm is the same as previously used. The program assumes first that I' = 1, then calculates  $\gamma_1$  as  $\gamma_{10}$  at ionic strength I', and obtains [Na<sup>+</sup>] from the equation:

$$[\text{Na}^+] (\gamma_{10}')^2 = (m_1 + 2 m_2 + m_3) (\gamma_{12})^2 \quad (24)$$

where

- [Na<sup>+</sup>] = the hypothetical concentration of free sodium ion
- $\gamma_{10}'$  = the mean activity coefficient of pure NaCl solution at ionic strength, I'
- I' = definition given below
- $m_1, m_2$ , and  $m_3$  = the molal concentrations of NaCl, Na<sub>2</sub>CO<sub>3</sub>, and NaHCO<sub>3</sub>, respectively, in the multicomponent electrolyte
- $\gamma_{12}$  = the mean activity coefficient of NaCl in this electrolyte, as measured by our amalgam electrode cell.

Table IX. Computer Program /XPYT/ for Ion-Pairing Calculation

```

1.1 TYPE "EXTENDED PYTKOWICZ FOR NA2CO3-NAHCO3 - 4/6/73
    SALT: CARB OR BICARB, AUTO INCR: YES OR NO, INPUT: K, A, L, OR NO"
1.2 CAR = 0, BIC = 2, YES = 1, NO = 99, K = 4, A = 3, L = 5, IND=1
1.25 DEMAND SAL, AUT, INP
1.26 AUT = NO IF INP = L
1.3 TO PART INP
1.4 TO STEP 1.2 IF INP<5
1.5 TO PART 99

3.10 TYPE "NACL-NA2CO3, K FROM ALPHA-12" IF SAL = CAR
3.101 TYPE "NACL-NAHCO3, K FROM ALPHA-12" IF SAL = BIC
3.11 DEMAND A12, J, LK1, DEL, KDP, KPR
3.14 DEMAND M1, PH UNLESS INP = L
3.15 DEMAND I, X1, PH, L12 IF INP=L
3.152 M1=X1*I, L12=L12+DEL IF INP = L
3.155 M = I, IPR = I
3.16 DO PART 10
3.17 G1P = G10, L1P = L10
3.21 M2 = (I - M1)/3, CO3 = M2 IF SAL = CAR
3.211 M2 = I - M1, HCO = M2 IF SAL = BIC
3.22 L12 = L10 - A12*3*M2 IF SAL = CAR AND INP = A
3.221 L12 = L10 - A12*M2 IF SAL = BIC AND INP = A
3.225 TYPE "
    [NA+]    [NAHCO3]  [HCO3-]  [CO3=]    I'          K*      LOG G1' "
    IF SAL = BIC
3.23 G12 = 10^L12, KF = 10^(LK1-PH)
3.24 TYPE IN FORM 31: M2, L12, G12, L10
3.255 TYPE "
    [NA+]    [NAC03-]  [CO3=]    [HCO3-]    J'          K*      LOG G1' "
    IF SAL = CAR
3.26 TO STEP 12.1 IF M2 = 0
3.30 IPP = IPR
3.31 DO PART 33 IF SAL = CAR
3.32 DO PART 34 IF SAL = BIC
3.40 M = IPR
3.41 DO PART 10
3.42 G1P = G10, L1P = L10
3.44 TO STEP 3.30 IF ABS(IPR-IPP) > 10^-5
3.45 LKS = LOG10(KS)
3.46 TYPE LKS
3.51 LINE
3.515 TO STEP 3.14 IF AUT = NO
3.52 M1 = M1 + .2*I
3.53 TYPE M1
3.54 TO STEP 3.15
3.55 TO STEP 1.2 IF M1>I

```

Table IX (Cont.)

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4.10 TYPE "NACL-NAHC03, ALPHA-12 FROM K" IF SAL=CAP
4.101 TYPE "NACL-NAHC03, ALPHA-12 FROM K" IF SAL = RIC
4.11 DEMAND I, LK1, DEL, KDP, KPR
4.20 DEMAND M1, PH
4.21 M2=(I-M1)/3, KF=10^(LK1-PH) IF SAL = CAR
4.211 M2=I-M1, KF= 10^(LK1-PH) IF SAL = RIC
4.215 TYPE M2
4.216 TO STEP 12.1 IF M2 = 0
4.22 RR =KPR+KDP*KF, AA=(1+KF)*RR, PR=1+KF+(M1+M2)*RR, CC=-M2
4.221 AA=AA/KF^2, PR=(1+KF+M1*PR)/KF IF SAL = RIC
4.225 DO PART 11
4.23 C03=X, HCO=KF*C03, NA=M1+M2+C03-HCO, NAC=M2-C03-HCO*(1+KDP*NA),
      IPR = M1+M2+2*C03+HCO*(1+KDP*NA)/2 IF SAL = CAR
4.231 HCO=X, C03=HCO/KF, NA=M1+HCO+C03, NAH=M2-HCO-C03*(1+KPR*NA),
      IPR=M1+2*C03+(M2+HCO-NAH)/2 IF SAL = RIC
4.30 M = IPR, INDEX = 1
4.31 DO PART 10
4.32 GIP = G10, L10 = L10
4.33 L12 = L10 + .5*LOG10(NA/(M1+2*M2)) IF SAL = CAR
4.331 L12 = L10 + .5*LOG10(NA/(M1+M2)) IF SAL = RIC
4.40 M = I
4.41 DO PART 10
4.42 DLG = L10 - L12
4.43 A12 = DLG/(3*M2) IF SAL = CAR
4.431 A12 = DLG/M2 IF SAL = RIC
4.44 TYPE IN FORM 44: IPR
4.45 TYPE "
      [NA+]      [NAC03]  [C03]      DLG      A12      L12      L10      LIP"
      IF SAL = CAR
4.46
4.461 TYPE "
      [NA+]      [NAHC03] [HCO3]    DLG      A12      L12      L10      LIP"
      IF SAL = RIC
4.50 TYPE IN FORM 45: NA, NAC, C03, DLG, A12, L12, L10, LIP IF SAL=CAR
4.501 TYPE IN FORM 45: NA, NAH, HCO, DLG, A12, L12, L10, LIP IF SAL = RIC
4.51 TYPE L12-DEL
4.52 TYPE "ASSUMING J'=J"
4.53 DLG = .5*LOG10(1+KPR*C03) IF SAL = CAR
4.531 DLG = .5*LOG10(1+KDP*HCO) IF SAL = RIC
4.54 A12 = DLG/(3*M2) IF SAL = CAR
4.541 A12 = DLG/M2 IF SAL = RIC
4.55 L12 = L10-DLG, L1P = L10
4.56 TYPE IN FORM 45: NA, NAC, C03, DLG, A12, L12, L10, LIP IF SAL = CAR
4.561 TYPE IN FORM 45: NA, NAH, HCO, DLG, A12, L12, L10, LIP IF SAL = RIC
4.57 LINE
4.575 TO STEP 4.20 IF AUT = NO
4.58 M1 = M1 + .2*J
4.59 TYPE M1
4.60 TO STEP 4.21 IF M1<J
4.61 TO STEP 4.10

```

Table IX (Cont.)

5.10 TYPE "NACL-NA2CO3, K FROM GAMMA 12" IF SAL = CAR  
 5.101 TYPE "NACL-NAHCO3, K FROM GAMMA 12" IF SAL = BIC  
 5.11 DEMAND LK1,DEL,KDP,KPR  
 5.12 TO STEP 3.15

10.1 S=-1.17082, SQM = SQRT(M)  
 10.2 LNG = S\*SQM/(1+1.5\*SQM)+.03684\*M+.01581\*M^2-.0008695\*M^3  
 10.3 G10 = EXP(LNG)  
 10.4 L10 = LNG/2.30258  
 10.45 DONE IF INDEX = 1  
 10.5 TYPE IN FORM 10: M , G10, L10

11.1 DIS = ABS(4\*CC\*AA/BB^2)  
 11.20 X = 0.5\*(-BB+SQRT(BB^2-4\*AA\*CC))/AA  
 11.22 TO STEP 11.99 IF DIS >.01  
 11.50 X0= -CC, CNT = 0  
 11.60 X1=(-CC-AA\*X0^2)/BB  
 11.61 TO STEP 11.70 IF ABS(X1-X0) < 10^-5\*X0  
 11.62 X0 = X1, CNT = CNT+1  
 11.63 TO STEP 11.60 IF CNT<100  
 11.70 X = X1  
 11.71 DONE IF CNT<10  
 11.72 TYPE IN FORM 11: X,CNT  
 11.99 DONE

12.1 NA=M1,NAC=0, CO3=0,HCO=0,NAH=0,IPR=M1,KS=0,M = M1  
 12.2 DO PART 10 FOR INDEX = 1  
 12.3 LIP=L10  
 12.4 TO STEP 3.50 IF INP = 3 OR INP = 5  
 12.5 DLG=0,A12=0,L12=L10  
 12.52 DO STEP 4.44  
 12.55 TO STEP 4.56 IF INP = 4  
 12.6 TO STEP 1.2

33.1 NA = (M1+2\*M2)\*(G12/GIP)^2, HCO = KF\*CO3  
 33.2 NAC = (M1 + 2\*M2) - NA\*(1 + KDP\*HCO)  
 33.3 CO3 = NA - M1 - M2 - HCO  
 33.4 IPR = M1 + M2 + 2\*CO3 + HCO\*(1+KDP\*NA)/2  
 33.5 KS = NAC/(NA\*CO3)  
 33.6 TYPE IN FORM 33: NA, NAC, CO3,HCO, IPR, KS, LIP

34.1 NA =(M1+M2)\*(G12/GIP)^2, CO3 = HCO/KF  
 34.2 NAH= M1+M2 - NA\*(1+KPR\*CO3)  
 34.3 HCO= NA-M1-CO3  
 34.4 IPR = M1+2\*CO3+(M2+HCO-NAH)/2  
 34.5 KS = NAH/(NA\*HCO)  
 34.6 TYPE IN FORM 33: NA, NAH, HCO, CO3, IPR, KS, LIP

Table IX (Cont.)

99.0 TYPE "DONE"

FORM 10:

M1= ZZ.ZZZZ , G10 = ZZ.ZZZZ, L10 = ZZ.ZZZZ

FORM 11:

LONG ITERATION-- X= ZZZZ.ZZZZZZ, ZZZZ CYCLES

FORM 31:

M2= ZZ.ZZZZZ, L12= ZZ.ZZZZZ, G12= ZZ.ZZZZZZ, L10 = ZZ.ZZZZZ

FORM 33:

ZZ.ZZZZZ ZZ.ZZZZZ ZZ.ZZZZZ ZZ.ZZZZZ ZZ.ZZZZZ ZZZZZZ.ZZZZZ ZZ.ZZZZZ

FORM 44:

CALCULATED I' = ZZ.ZZZZZ

FORM 45:

ZZ.ZZZZZ ZZ.ZZZZZ ZZ.ZZZZZ ZZ.ZZZZZ ZZ.ZZZZZ ZZ.ZZZZZ ZZ.ZZZZZ ZZ.ZZZZZ

DO PART 1

EXTENDED PYTKOWICZ FOR NaCl-NA2CO3-NAHCO3 - 3/19/70

SALT: CARB OR BICARB, AUTO INCR: YES OR NO, INPUT: K, A, L, OR NO

SAL = BIC AUT = NO INP = L

NaCl-NAHCO3, K FROM GAMMA 12

LKI = 9.8 DEL = .0022 KDP = 10<sup>-5</sup> KPR = 10<sup>+5</sup>

I = .5073 X1 = .7486 PH = 8.83 L12 = -.1770

[NA+]	[NAHCO3]	[HCO3-]	[CO3=]	I'	K*	LOG G1
M2= 7.12754,	L12= -0.17480,	G12= 0.668652,	L10 = -0.16526			
0.48550	0.00082	0.09207	0.01367	0.51649	0.01832	-0.1653
0.48673	0.00538	0.09710	0.00987	0.50912	0.11387	-0.1658
0.48575	0.00557	0.09558	0.01040	0.50935	0.11997	-0.1654
0.48578	0.00579	0.09577	0.01024	0.50901	0.12446	-0.1654
0.48573	0.00581	0.09570	0.01026	0.50901	0.12489	-0.1654
LKS =		-0.90347019				

DO PART 1

EXTENDED PYTKOWICZ FOR NaCl-NA2CO3-NAHCO3 - 3/19/70

SALT: CARB OR BICARB, AUTO INCR: YES OR NO, INPUT: K, A, L, OR NO

SAL = CAR AUT = YES INP = K

NaCl-NA2CO3, ALPHA-12 FROM K

I = 1.0 LKI = 9.75 DEL = .0015 KDP = 10<sup>-6.67</sup>KPR = 10<sup>+3.7</sup>

M1 = 0

PH = 10.9

M2 = 0.33333333

CALCULATED I' = 0.63754

[NA+]	[NA2CO3]	[CO3]	DLG	A12	L12	L10	L1P
0.47197	0.17251	0.14920	0.0650	0.06504	-0.24635	-0.1809	-0.17185
L12-DEL =		-0.24834547					
ASSUMING I'=1							
0.47197	0.17251	0.14920	0.0651	0.06513	-0.24603	-0.1809	-0.18090

The rest of the model follows a straightforward equilibrium treatment. The ionic strength is defined in terms of the free concentrations at equilibrium:

$$I' = \frac{1}{2} \{ [Na^+] + [Cl^-] + [HCO_3^-] + 4[CO_3^{2-}] + [NaCO_3^-] \} \quad (25)$$

which are in turn defined by the mass balances and equilibrium relationships:

$$m_1 = [Cl^-] \quad (26)$$

$$m_1 + 2m_2 + m_3 = [Na^+] + [NaHCO_3] + [NaCO_3^-] \quad (27)$$

$$m_2 + m_3 = [HCO_3^-] + [CO_3^{2-}] + [NaHCO_3] + [NaCO_3^-] \quad (28)$$

$$[HCO_3^-] = K_1 [H^+] [CO_3^{2-}] \quad (29)$$

$$[NaHCO_3] = K_1'' [Na^+] [HCO_3^-] \quad (30)$$

$$[NaCO_3^-] = K_1' [Na^+] [CO_3^{2-}] \quad (31)$$

It is from these that the other concentrations are obtained, using parts 33(carbonate) or 34(bicarbonate). Note that provision has been made for adding an increment DEL to  $\log \gamma_{12}$ , and that preliminary values of  $K_1'$ (KPR) and  $K_1''$ (KDP) are needed, along with the protonation equilibrium constant  $K_1$  [LK1 =  $\log(K_1)$ ].

This mode of calculation requires, therefore, that several iterations be made using revised estimates of  $K_1'$  and  $K_1''$ . Since such a revision involves assessment of the whole body of data and some judgment about the best values of the constants, the iteration of these quantities has been left to the operator of the program. However, a more mechanical iteration to find the best value of  $I'$  is included in the program, and each approximation is printed out. This time-consuming printing can be suppressed by a conditional statement at 33.55 and 34.55, e.g., "DONE IF ABS(IPR-IPP) > 10<sup>-5</sup>, " or, simply, "DONE" if only the equilibrium constant is desired.

Part 4 does the inverse calculation, generating a curve of  $\log \gamma_{12}$  or  $\alpha_{12}$  versus composition once the ion-pairing constants are known. In this part, the mass balances and equilibria have been combined to yield a quadratic of the form.

$$ax^2 + bx + c = 0 \quad (32)$$

where, for  $x = [CO_3^{2-}]$ , the coefficients are

$$a = (1 + K_1 [H^+]) (K_1' + K_1'' K_1 [H^+]) \quad (33)$$

$$b = 1 + K_1 [H^+] + (m_1 + m_2) (K_1' + K_1'' K_1 [H^+])$$

$$c = -(m_2 + m_3)$$

and for  $x = [\text{HCO}_3^-]$ , the coefficients are

$$a = (1 + K_1 [\text{H}^+]) (K_1' + K_1' K_1 [\text{H}^+]) / (K_1 [\text{H}^+])^2 \quad (34)$$

$$b = \{ 1 + K_1 [\text{H}^+] + (m_1 + m_2) (K_1' + K_1' K_1 [\text{H}^+]) / (K_1 [\text{H}^+]) \}$$

$$c = -(m_2 + m_3)$$

To obtain the most accurate solution, the variable  $x$  is chosen to be  $[\text{CO}_3^{2-}]$  when the second salt is  $\text{Na}_2\text{CO}_3$ , and  $[\text{HCO}_3^-]$  when the second salt is  $\text{NaHCO}_3$ , but in principle the two choices lead to the same answers. The quadratic is solved by the subroutine of part 11, in which provision is made for the situation where the quadratic term is very small, when the usual quadratic formula can lead to large rounding-off errors. Note that  $m_3 = 0$  and  $m_2 = m$  if  $\text{SAL} = \text{CAR}$ , and  $m_2 = 0$  and  $m_3 = m$  if  $\text{SAL} = \text{BIC}$ . Eqs. (33) and (34), however, are general.

Provision is also made for calculating  $\log \gamma_{12}$  according to the approximate equation (which assumes  $I' = I$ ) published by Pytkowicz and Kester.<sup>25</sup> Although this gives a curve of approximately the same shape, the values of  $\gamma_{12}$  obtained are not in agreement with the more rigorous calculation, and, to fit the data, the ion-pairing constants must be changed.

Note that part 10 is a subroutine to calculate the mean activity coefficient of  $\text{NaCl}$ , and does not give quite the same values as the Robinson and Stokes tables.<sup>12</sup> Some adjustment is required to match the calculated curves with the experimental data, since the reference value of  $\gamma_{10}$  in the experiments was taken from the Robinson and Stokes tables. This adjustment is made with the parameter  $\text{DEFI}$ , although a more satisfactory method would have been to recompute the parameters of the equation in step 10.2 to fit the Robinson and Stokes data. The equation in step 10.2 is taken from the report by R. M. Rush (ORNL-4402).<sup>7</sup> Part 12 takes care of the case  $m_2 = 0$ , when most of the complicated calculations can be dispensed with. An example of the output from the program is given at the end of Table IX.

The results of the calculations are summarized in Tables X and XI. In the first approximation, we assumed values for the ion-pairing constants which we calculated previously without taking account of the protonation equilibria:  $\log K_1' = -0.5$  and  $\log K_1' = +0.5$ . This yielded second approximations which were considerably different. The average values and 95% confidence limits are given in Table XII, and the individual data points are given in Tables X and XI. A third approximation gave no change in  $K_1'$ , but made a substantial change in  $K_1'$ , particularly at  $I = 1.0$ . A fourth approximation did not change any of the constants.

Curves calculated using the extended model are not qualitatively different from those obtained with the single-equilibrium models given in the Second Interim Report. As we pointed out previously, the deviation of calculated values from experimental seems to be somewhat less for Harned's rule, but the differences are not great. Fig. 5 shows a comparison for  $\text{NaCl-NaHCO}_3$  electrolytes at  $I = 1.0\text{m}$ . Here, it is important to notice how strongly the  $\text{pH}$  affects the calculated curve. This is a result of replacing weak  $\text{Na}^+ - \text{HCO}_3^-$  ion pairs with the relatively



Table X. Ion-Pairing Constants From Activity Coefficients in NaCl-NaHCO<sub>3</sub> Electrolytes at 25 °C\*

I	X <sub>1</sub>	pH	log $\gamma_{12}$		log K <sub>1</sub> "			
			log K <sub>1</sub> "	= 9.8	9.8	9.8	9.8	
			log K <sub>1</sub> "	= -0.5	-0.5	-0.547	-0.412	
			log K <sub>1</sub> "	= +0.5	+0.5	+0.140	+0.141	
			$\Delta$	= 0	0.0022	0.0022	0.0022	
0.5073	0.7486	8.83	-0.1791	-0.322	-0.543	-0.303	-0.303	
			-0.1770	-0.532	-0.903	-0.474	-0.475	
0.5133	0.5055	8.18	-0.1782	-0.645	-0.791	-0.680	-0.680	
			-0.1795	-0.574	-0.700	-0.608	-0.608	
0.5215	0.1793	8.21	-0.2092	-0.141	-0.178	-0.146	-0.146	
			-0.2117	-0.101	-0.137	-0.107	-0.107	
0.5240	0.0761	8.22	-0.1974	-0.454	-0.506	-0.440	-0.440	
			-0.1932	-0.559	-0.623	-0.537	-0.538	
			log K <sub>1</sub> "	= 9.75	9.75	9.75	9.75	
			log K <sub>1</sub> "	= -0.5	-0.5	-0.862	-0.670	
			log K <sub>1</sub> "	= +0.5	+0.5	+0.268	+0.271	
			$\Delta$	= 0	0.0020	0.0020	0.0020	
1.0400	0.4122	8.6	-0.2102	-1.009	-1.167	-0.786	-0.789	
			-0.2109	-0.963	-1.108	-0.759	-0.761	
1.0115	0.1135	8.4	-0.2225	-0.752	-0.808	-0.663	-0.664	
			-0.2234	-0.729	-0.782	-0.645	-0.646	
1.0049	0.0444	8.2	-0.2255	-0.632	-0.671	-0.598	-0.599	
			-0.2272	-0.602	-0.638	-0.570	-0.571	

\* Notes: These data are the same as reported for the AgCl-Na(lig) cell in the second interim report, page 24. Note that the third pH entry is 8.18, not 9.18.

In headings of log K<sub>1</sub>" are given the assumed values of parameters needed to calculate the constant.  $\Delta$  is an increment to log  $\gamma_{12}$  to account for the discrepancy between the Robinson & Stokes<sup>12</sup> tables originally used to calculate log  $\gamma_{10}$  for the reference solution and the corresponding log  $\gamma_{10}$  value obtained from the Rush equation<sup>7</sup> used in the computer program.

Table XI. Ion-Pairing Constants From Activity Coefficients in NaCl-Na<sub>2</sub>CO<sub>3</sub> Electrolytes at 25 °C\*

I	X <sub>1</sub>	pH	log γ <sub>12</sub>		log K <sub>1</sub> <sup>'</sup>	
			log K <sub>1</sub>	= 9.8	9.8	9.8
			log K <sub>1</sub> <sup>"</sup>	= -0.5	-0.5	-0.547
			log K <sub>1</sub> <sup>'</sup>	= +0.5	+0.5	+0.140
			Δ	= 0	0.0020	0.0020
0.5575	0.9096	10.24	-0.1707	+0.485	-0.366?	-0.354?
			-0.1718	+0.902	+0.167	+0.172
0.5062	0.4868	10.89	-0.1817	+0.417	+0.314	+0.315
			-0.1789	+0.272	+0.164	+0.164
0.4699	0.1880	11.07	-0.1794	+0.074	0.000	+0.000
			-0.1761	-0.053	-0.142	-0.141
0.4585	0.0944	10.99	-0.1893	+0.329	+0.277	+0.278
			-0.1865	+0.255	+0.201	+0.202
			log K <sub>1</sub>	= 9.75	9.75	9.75
			log K <sub>1</sub> <sup>"</sup>	= -0.5	-0.5	-0.862
			log K <sub>1</sub> <sup>'</sup>	= +0.5	+0.5	+0.268
			Δ	= 0	0.0019	0.0019
1.0092	0.5069	10.1	-0.2085		+0.572?	+0.582?
			-0.2076		+0.526?	+0.538?
0.9923	0.1357	10.8	-0.2265		+0.316	+0.319
			-0.2240		+0.260	+0.265
0.9883	0.0483	10.9	-0.2301		+0.274	+0.277
			-0.2273		+0.220	+0.224

\* These data are the same as reported for the AgCl-Na (Hg) cell in the second interim report, page 27. See notes to Table X. Points marked "?" were not included in computing averages or confidence limits for Table XII.

Table XI (Cont.)

			$\log K_{1,0}$	$\tau$	9.63	9.63	9.63
			$\log K_{1,1}$	$=$	-0.5	-0.5	-0.862
			$\log K_1$	$\tau$	+0.5	+0.5	+0.373
			$\Delta$	$=$	0	0.0014	0.0014
3.0247	0.7459	10.98	-0.1845	(negative K)			
			-0.1786	+0.584	+0.418	+0.419	
2.9973	0.4831	11.15	-0.2112	+0.350	+0.297	+0.298	
			-0.2104	+0.320	+0.270	+0.270	
2.9762	0.2621	11.00	-0.2475	+0.508	+0.470	+0.470	
			-0.2466	+0.483	+0.446	+0.447	
2.9523	0.0532	11.35	-0.2715	+0.338	+0.318	+0.319	
			-0.2692	+0.305	+0.286	+0.286	
2.8762	0.0458	11.2	-0.2797	+0.460	+0.436	+0.437	
			-0.2784	+0.438	+0.416	+0.416	

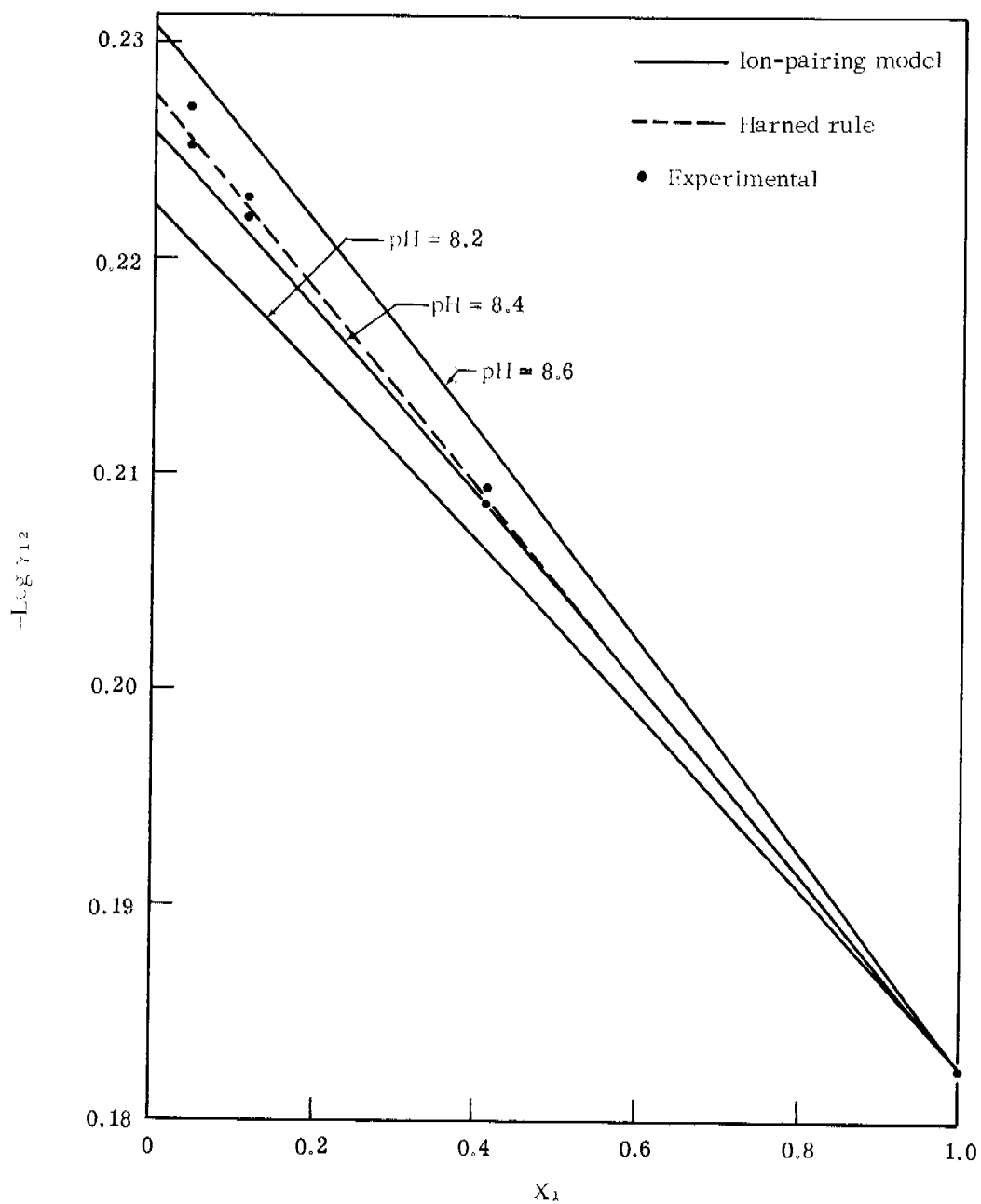


Fig. 5. Fit of ion-pairing model to amalgam electrode data for NaCl-NaHCO<sub>3</sub> at  $l = 1.0$  (parameters:  $\alpha_{12} = 0.045$ ,  $\log K'_1 = +0.27$ ,  $\log K'_2 = -0.67$ ,  $\log K_1 = 9.75$ , pH as indicated)

strong  $\text{Na}^+ - \text{CO}_3^{2-}$  ion pairs as the pH increases. The stronger ion pairs remove more  $\text{Na}^+$  from the equilibrium solution and thus increase the slope of the curve.

A general comment might be made at this point. Formally, any two-salt electrolyte mixture which displays a positive Harned rule coefficient for one salt can be described by a model in which the second salt is ion paired. As long as the ion pairing is relatively weak, and the effective ionic strength of the solution is not too much diminished by the ion-pairing process, the curve calculated from the ion-pairing model will be quite close to the straight line predicted by Harned's rule.

Two important points should be borne in mind, however. First, the assumption that all deviations from constant activity at constant ionic strength are due to a simple equilibrium of ion pairing is certainly not correct, since this does not distinguish between size effects and other nonlinear, electrostatic effects, and a more definite type of ion pairing which obeys the law of mass action. This is most obvious in the failure of ion pairing alone to give a consistent model of deviations from the Debye-Hückel equations in the case of a single salt component.

Second, negative values for Harned rule coefficients (which one finds in many systems) indicate that ion pairing of the salt whose activity is being measured is stronger than that of the other salt (e.g., a negative  $\alpha_{12}$  means stronger ion pairing between  $\text{Na}^+$  and  $\text{Cl}^-$  than between  $\text{Li}^+$  and  $\text{Cl}^-$ ), and thus it is clear that this model can only give the extent of ion pairing of one salt compared with another. We have made the tacit assumption that  $\text{NaCl}$  is nonassociated, but conductance studies at high concentrations have suggested that there may be a rather substantial degree of association<sup>6,6</sup> between  $\text{Na}^+$  and  $\text{Cl}^-$ . We therefore know this is only an approximation. The ion pairing of  $\text{Na}^+$  with carbonate or bicarbonate as expressed by the equilibrium constants we have calculated is thus shown only to be stronger than the ion pairing of  $\text{Na}^+$  with  $\text{Cl}^-$ .

Now, let us turn to the comparison of our ion-pairing constants with those obtained by other methods. The two other important attempts to assess the ion pairing between sodium and carbonate species have been the work of Garrels, et al.,<sup>30</sup> which has been discussed in the Second Interim Report, and the recent work of Nakayama.<sup>29</sup> Garrels' basic assumption was that Walker-Bray-Johnson values<sup>27</sup> for the activity coefficients of  $\text{KHCO}_3$  could be used to calculate the ion pairing in  $\text{NaHCO}_3$  by assuming that  $\text{KHCO}_3$  was not ion paired at all. The connection with  $\text{Na}_2\text{CO}_3$  was made by means of the MacInnes assumption,  $\gamma_K = \gamma_{\text{Cl}^-}$ , and the protonation equilibria of the carbonate ion. One may thus treat Garrels' value as being (in a rather complicated way) corrected to zero ionic strength.

Nakayama<sup>29</sup> worked directly from data on the protonation equilibria at low ionic strengths of  $\text{NaCl}$ , calculating activity coefficients from an extended Debye-Hückel relation, and attributing the remainder of the salt effect to ion pairing of carbonate species with  $\text{Na}^+$ . His constants, also, are thus corrected to zero ionic strength. Both the Garrels and Nakayama values are listed in Table XII.

Since our measurements were made at constant formal ionic strength, we have chosen to use  $\text{NaCl}$  at that ionic strength as our reference state, and the relation between our

Table XII. Summary of Ion-Pairing Constants with 95% Confidence Limits

I =	log K <sub>1</sub> <sup>"</sup>		log K <sub>1</sub> <sup>'</sup>		
	0.5	1.0	0.5	1.0	3.0
Previous estimate*	-0.50 <sub>±.15</sub>	-0.50 <sub>±.05</sub>	+0.15 <sub>±.07</sub>	+0.40 <sub>±.06</sub>	+0.47 <sub>±.13</sub>
First guess	-0.5	-0.5	+0.5	+0.5	+0.5
2nd approx.	-0.55 <sub>±.24</sub>	-0.86 <sub>±.26</sub>	+0.14 <sub>±.16</sub>	+0.27 <sub>±.07</sub>	+0.37 <sub>±.06</sub>
3rd approx.	-0.41 <sub>±.19</sub>	-0.67 <sub>±.10</sub>	+0.14 <sub>±.16</sub>	+0.27 <sub>±.07</sub>	+0.37 <sub>±.06</sub>
4th approx	-0.41 <sub>±.19</sub>	-0.67 <sub>±.10</sub>	+0.14 <sub>±.16</sub>	+0.27 <sub>±.07</sub>	+0.37 <sub>±.06</sub>
Garrels <sup>30</sup> (I→0)		-0.26		+1.27	
Nakayama <sup>29</sup> (I→0)		+0.16 <sub>±.06</sub>		+0.55	
This work (I→0)	-0.08 <sub>±.23</sub>	-0.30 <sub>±.13</sub>	+0.77 <sub>±.18</sub>	+0.96 <sub>±.13</sub>	+0.97 <sub>±.23</sub>
"Best values"	-.24 <sub>±.24</sub>		+0.91 <sub>±.32</sub>		

\*Not including effect of  $\text{HCO}_3^-$  on  $\text{NaCO}_3^-$  ion pairing or effect of  $\text{CO}_3^{=}$  on  $\text{NaHCO}_3$  ion pairing. Other calculations made including all three equilibria as described in the text. Our estimate at  $I \rightarrow 0$  made from fourth approximation values, using data in Table XIII.

reference state, and the relation between our "concentration" equilibrium constants and the zero-ionic-strength constants of the other workers must be made by means of some ad hoc assumptions regarding the activity coefficients of individual ionic species (or, more rigorously, the mean activity coefficients of unmeasurable combinations of ions). This sort of assumption can be quite uncertain at the high ionic strengths we have been studying, and we will attempt to make our assumptions as explicit as possible.

In order to demonstrate the wide range of possible estimates for single-ion activity coefficients, we have collected in Table XIII some estimates for the activity coefficients of the ions with which we are concerned in this project. For  $\text{Na}^+$  and  $\text{H}^+$ , the mean activity coefficient of the chloride is the only simple alternative to the MacInnes assumption. For the bicarbonate and carbonate ions, we do not even have mean activities of an alkali metal salt, but only the individual ionic activities calculated by Walker, Bray and Johnson.<sup>27</sup> It is interesting to note that their estimate of  $\gamma$  for  $\text{HCO}_3^-$  is almost identical to the observed mean activity coefficient of  $\text{NaCl}$ . Their estimate for the carbonate ion is not too different from  $\gamma_{\pm}^2$  for  $\text{CaCl}_2$ , an electrolyte believed to be essentially nonassociated (at least to the extent that  $\text{NaCl}$  is nonassociated), but not in such good agreement with the MacInnes estimate<sup>67</sup> of  $\gamma$  for  $\text{Ca}^{2+}$ . We have also included estimates made using the Debye-Hückel equation with the Kielland<sup>8</sup> ion-size parameters, as well as the Davies equation. There is moderate agreement at  $I = 0.5$  with the Davies equation, but these equations are useless predictors of  $\gamma$  at higher ionic strengths, as has often been shown.

For our calculations, we have chosen as best estimates the values listed in Table XIII, and have assumed confidence limits for error analysis as noted below:

- $\text{Na}^+$  — Mean of  $\text{NaCl}$  and MacInnes. Range taken as confidence limits.
- $\text{H}^+$  — Mean of  $\text{HCl}$  and MacInnes. Range taken as confidence limits.
- $\text{HCO}_3^-$  — Walker value. Confidence limits same as  $\text{Na}^+$ .
- $\text{CO}_3^{2-}$  — Square of  $\gamma_{\pm}$  for  $\text{CaCl}_2$ . Upper range, MacInnes  $\text{Ca}^{2+}$ ; lower range, Walker  $\text{CO}_3^{2-}$  value.
- $\text{NaCO}_3^-$  — Same as  $\text{HCO}_3^-$ . Confidence limits taken to be twice those for  $\text{Na}^+$ .
- $\text{NaHCO}_3$  —  $\gamma = 1.00$ , since it is uncharged. Confidence limits twice those for  $\text{Na}^+$ .

Using these values, the constants in Table XII were corrected to  $I = 0$  by means of the equations

$$\log K_1' (I \rightarrow 0) = \log K_1' + \log (\gamma_{\text{NaCO}_3}) - \log (\gamma_{\text{Na}} \gamma_{\text{CO}_3}) \quad (35)$$

$$\log K_1'' (I \rightarrow 0) = \log K_1'' + \log (\gamma_{\text{NaHCO}_3}) - \log (\gamma_{\text{Na}} \gamma_{\text{HCO}_3}) \quad (36)$$

The variances of the activity coefficients were assumed to be proportional to the squares of the confidence limits in Table XIII, and were assumed to be additive. The "best estimates" in Table XII were obtained as a weighted average of the values obtained at different ionic strengths, with the weighting factors taken to be the reciprocal of the variances.

Table XIII. Estimates of Individual Ionic Activity Coefficients

Ion	Method	log $\gamma$				
		I =	0.1	0.5	1.0	3.0
$H^+$	$\gamma_+$ (HCl)		-0.0991	-0.1209	-0.0920	+0.1193
	Mac Innes		-0.0846	-0.0542	+0.0351	+0.4836
	Debye-Huckel, $a=9$		-0.083	-0.117	-0.129	-0.144
	Best estimate		-0.092 $\pm$ .007	-0.087 $\pm$ .033	-0.064 $\pm$ .029	+0.30 $\pm$ .18
$Na^+$	$\gamma_+$ (NaCl)		-0.1088	-0.1668	-0.1825	-0.1465
	Mac Innes		-0.1040	-0.1460	-0.1459	-0.0480
	Debye-Huckel, $a=4$		-0.114	-0.188	-0.220	-0.269
	Davies		-0.121	-0.160	-0.153	-0.018
	Best estimate		-0.106 $\pm$ .003	-0.156 $\pm$ .010	-0.164 $\pm$ 0.018	-0.097 $\pm$ 0.049
$HCO_3^-$	Walker (KHCO <sub>3</sub> )		-0.102	-0.166	-0.184	-0.210
	Best estimate		-0.102 $\pm$ .003	-0.166 $\pm$ .010	-0.184 $\pm$ .018	-0.210 $\pm$ .049
$CO_3^{2-}$	Walker (K <sub>2</sub> CO <sub>3</sub> )		-0.410	-0.640	-0.738	-0.848
	$[\gamma_+ (CaCl_2)]^2$		-0.4120	-0.6302	-0.6898	-0.6020
	Mac Innes-CaCl <sub>2</sub>		-0.3908	-0.5701	-0.5965	-0.4130
	Debye-Huckel, $a=5$		-0.424	-0.667	-0.875	-0.917
	Davies		-0.484	-0.639	-0.610	-0.071
	Best estimate		-0.40 $\pm$ .02	-0.613 $\pm$ .043	-0.675 $\pm$ .078	-0.62 $\pm$ .22
$NaCO_3^-$	Best estimate		-0.10 $\pm$ .01	-0.16 $\pm$ .02	-0.16 $\pm$ .04	-0.10 $\pm$ .10
$NaHCO_3$ or $H_2CO_3$	Best estimate		0.00 $\pm$ .01	0.00 $\pm$ .02	0.00 $\pm$ .04	0.00 $\pm$ .10



An attempt was made to calculate the ionic strength dependence of the protonation equilibrium constants  $K_1$  and  $K_{12}$ :

$$[ \text{HCO}_3^- ] = K_1 [ \text{H}^+ ] [ \text{CO}_3^{2-} ] \quad (37)$$

$$[ \text{H}_2\text{CO}_3 ] = K_{12} [ \text{H}^+ ] [ \text{HCO}_3^- ] \quad (38)$$

using the activity coefficient estimates in Table XIII together with the ion-pairing constants of Table XII. As described in the interim report, a concentration equilibrium constant measured by a method (e.g., potentiometric or spectrophotometric pH titration) which does not distinguish between  $\text{HCO}_3^-$  and  $\text{NaHCO}_3$  or between  $\text{CO}_3^{2-}$  and  $\text{NaCO}_3^-$  can be related to the "thermodynamic" equilibrium constant (i.e., for  $I = 0$ ) by the equations:

$$\log K_1 = \log K_1^0 + \log \left( \frac{\gamma_{\text{H}} \gamma_{\text{CO}_3}}{\gamma_{\text{HCO}_3}} \right) + \log \left( \frac{1 + K_1^{\text{II}} [\text{Na}^+]}{1 + K_1^{\text{I}} [\text{Na}^+]} \right) \quad (39)$$

$$\log K_{12} = \log K_{12}^0 + \log \left( \frac{\gamma_{\text{H}} \gamma_{\text{HCO}_3}}{\gamma_{\text{H}_2\text{CO}_3}} \right) - \log (1 + K_1^{\text{II}} [\text{Na}^+]) \quad (40)$$

Using our "best values" from Tables XII and XIII, we obtained the results given in Table XIV. Included in Table XV also are some estimates for  $K_1$  at low ionic strengths made from the pH of standard sodium carbonate-bicarbonate buffers<sup>13</sup> by means of the equation:

$$\log K_1 = \text{pH} + \log \gamma_{\text{H}} + \log (1 - K_1 K_{12} [ \text{H}^+ ]^2) - \log (1 + 2 K_{12} [ \text{H}^+ ]) \quad (41)$$

(A second approximation does not change  $K_1$ .) Here, we have assumed that the activity coefficient of  $\text{H}^+$  in the expression  $\text{pH} = -\log [ \text{H}^+ ] \gamma_{\text{H}}$  is given by the mean activity coefficient of  $\text{HCl}$  at the same ionic strength. This is consistent with the fact that the original measurements were made with the hydrogen-silver chloride cell and extrapolated to zero chloride concentration. To be rigorous, the mean activity coefficient of  $\text{HCl}$  in the carbonate medium should be used, but this is not known. Alternatively, the MacInnes assumption could be used (Table XII). This would give (at  $I = 0.1$ ) a value of  $\log \gamma_{\text{H}}$  which is 0.015 unit more positive, and hence a value of  $K_1$  which is 0.015 unit more positive. This alternative assumption gives some indication of the possible systematic error in such a calculation. To be most rigorous, one should go back to the original experimental data and recalculate them using the minimum of nonthermodynamic assumptions. We intend to do such calculations, encompassing all available literature data on the carbonate protonation equilibria, at some time in the future. We also intend to carry out further experiments to obtain  $K_1$  in the range from  $I = 0.1$  to 1.0, since this seems to be a critical region of interest.

In spite of the fact that we have not completely analyzed all the available literature data, we have summarized some of it in Table XVI, and have compared it with the calculated curves in Fig. 6. The various components of the calculated constants, together with their confidence limits,

Table XIV. Calculated Ionic Strength Dependence of Ion-Pairing and Protonation Equilibria in NaCl Medium

I	$\log K_1^*$	$\log K_1^{**}$	$\log K_1$	$\log K_{12}$
0	$0.91 \pm 0.32$	$-0.24 \pm 0.24$	$10.332 \pm 0.006^\dagger$	$6.356 \pm 0.004^\dagger$
0.1	$0.50 \pm 0.32$	$-0.45 \pm 0.24$	$9.84 \pm 0.09$	$6.15 \pm 0.02$
0.5	$0.30 \pm 0.32$	$-0.56 \pm 0.24$	$9.55 \pm 0.21$	$6.05 \pm 0.05$
0.5 $\ddagger$	$0.14 \pm 0.16$	$-0.41 \pm 0.19$	$9.65 \pm 0.11$	$6.03 \pm 0.05$
1.0	$0.23 \pm 0.33$	$-0.59 \pm 0.24$	$9.45 \pm 0.26$	$6.01 \pm 0.07$
1.0 $\ddagger$	$0.27 \pm 0.07$	$-0.67 \pm 0.10$	$9.40 \pm 0.11$	$6.02 \pm 0.06$
3.0	$0.30 \pm 0.40$	$-0.55 \pm 0.27$	$9.65 \pm 0.54$	$6.18 \pm 0.24$
3.0 $\ddagger$	$0.37 \pm 0.06$	$(-0.67 \pm 0.10)$	$9.53 \pm 0.30$	$6.23 \pm 0.22$

\*"Best Values" from Tables XII and XIII except where noted.

$\dagger$  Reference (29).

$\ddagger$  Using actual values for  $K_1^I$  and  $K_1^{II}$  (Table XII) at ionic strength indicated. At  $I = 3$ ,  $K_1^{II}$  assumed to be the same as at  $I = 1$ .

Table XV. Estimates of  $K_1$  at Low Ionic Strength From pH of Equimolar  $\text{NaHCO}_3$ - $\text{Na}_2\text{CO}_3$  Buffers

I	pH, at 25 °C*	$\log \gamma_H^\dagger$	$\log K_1$
0.04	10.112	-0.074	10.038
0.10	10.018	-0.099	9.918
0.20	9.933	-0.115	9.817

\*Ref. (13), p. 712.

$\dagger \gamma_{\pm}$  for HCl, Ref. (13), p. 716.

Table XVI. Data and References for Fig. 6

I	Medium	$\log K_1$	$\log K_{12}$	References
0	Extrap.	$10.332 \pm 0.006$	$5.356 \pm 0.004$	See Table XIV, footnote
0.1	NaCl		6.116	Ref. (68)
0.2	↓		6.056	Ref. (13), p. 760
0.5			5.982	
0.7			5.915	
1.0	↓		5.944	
1.0	NaCl	9.37		Ref. (46)
1.0	NaClO <sub>4</sub>	9.57	6.04	Ref. (40)
3.5	NaClO <sub>4</sub>	9.56	6.33	
0.26	KNO <sub>3</sub>		6.06	Ref. (42)
1.0	↓		5.99	
2.0	↓		5.97	
0.72	Sea water	9.23	6.13	Ref. (2), p. 53
0.7	Sea water		6.10	Ref. (47)

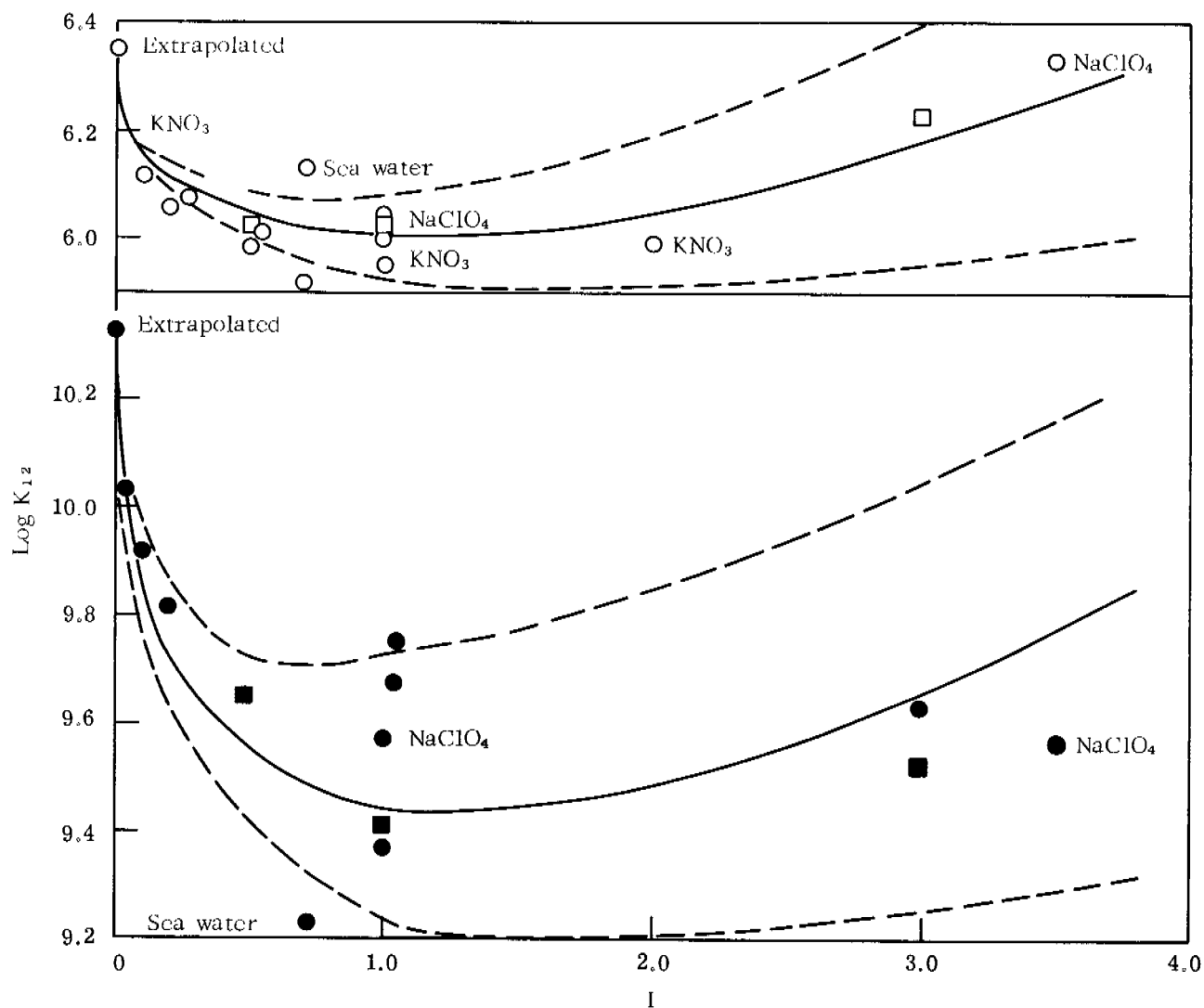


Fig. 6. Comparison of calculated and experimental ionic strength dependence of protonation equilibria (medium is NaCl, except where noted; dashed lines represent extremes of confidence limits; unbroken lines are based on zero ionic strength "best values" of  $K_1'$  and  $K_1''$  of Table XII and activity coefficients in Table XIII; data points ■ recorded using actual  $K_1'$  and  $K_1''$  values at indicated  $I$ )

are given in Table XVII. The dashed lines on Fig. 6 represent the extreme possibilities of error in the calculated values. Nearly all the observed and calculated values are in agreement within these limits, and perhaps this is all one can expect. The largest discrepancies are to be found in  $K_1$  at  $I = 1.0$ , where our potentiometric values and the spectrophotometric values of Bruckenstein and Nelson (both in 1.0M NaCl medium) disagree by 0.3 logarithmic unit. The reasons for this discrepancy should be investigated further. The difference may be due simply to the effect of NaCl on the activity coefficients of the indicator species — a salting-out effect — or may reflect an experimental error in one or both of the studies.

It is of interest to examine the sources of error in the calculated protonation constants (Table XVII) in more detail. With respect to the activity coefficients, the largest contribution comes from the estimated value for carbonate ion, and the next largest from hydrogen ion. The error due to the other monovalent or uncharged ions is quite small. The error in estimating the activity coefficient of  $H^+$  has sometimes been avoided by using "mixed" constants (with  $H^+$  activity instead of concentration in the equilibrium expression), but such constants cannot be determined with thermodynamic rigor (as can "concentration" constants), and thus provide their own source of confusion. With respect to the ion-pairing contribution, our interpolation procedure, which assumes that the thermodynamic ion-pairing constant is independent of ionic strength, does not change the calculated values of  $K_1$  or  $K_{12}$  by very much (+ on Fig. 6), but does introduce quite a bit of uncertainty into these values. Using the experimental  $K_1^0$  and  $K_2^0$  values instead of interpolated ones reduces this uncertainty by a factor of 3 or 4.

These observations only emphasize the desirability of working in a constant ionic medium and referring the thermodynamic values obtained to a standard state in that same medium. Most of the error in Fig. 6 and Table XVII comes in trying to relate a high ionic strength measurement to one extrapolated to infinite dilution.

In this connection, we should discuss the work of Nakayama<sup>29</sup> in which he recalculated previous measurements of carbonate protonation equilibria in  $Na^+$ -containing media, including contributions from the formation of the ion pairs  $NaHCO_3$  and  $NaCO_3^-$ . It is quite apparent from our own calculations on this system that the ion-pairing contribution to the variation of  $K_1$  and  $K_{12}$  is not a major effect. Looking at Table XVII, one can easily see that the terms  $B_1$  and  $B_2$ , which contain the ion-pairing effect, are actually the same order of magnitude as the activity coefficient terms at all ionic strengths. Furthermore, the cumulative uncertainty due to the activity coefficient terms is not much smaller than the ion-pairing effect. The result of this analysis is that the salt effect on protonation equilibria does not lead to accurate estimates of the ion-pairing constants, primarily because the activity coefficient variation has such a large and uncertain contribution to the effect.

Nakayama obtained activity coefficients from the extended Debye-Hückel equation, with Kielland's ion-size parameters,<sup>8</sup> and restricted his calculations to data obtained at ionic strengths below 0.05M. In this way, he hoped to minimize the random error from the activity coefficient contribution. However, his estimates of the error in his ion-pairing constants do

Table XVII. Components of Calculated Protonation Equilibria Constants and Their Confidence Limits

(logarithm of quantity indicated)								
I	$K_1^0$	$\gamma_H$	$\gamma_{CO_3}$	$\gamma_{HCO_3}$	$B_1$ <u>interpolated</u>	$K_1$	$B_1$ <u>actual</u>	$K_1$
0.1	10.332 $\pm .006$	-.092 $\pm .007$	-.400 $\pm .020$	-.102 $\pm .003$	-.10 $\pm .09$	9.84 $\pm .09$		
0.5	10.332 $\pm .006$	-.087 $\pm .033$	-.613 $\pm .043$	-.166 $\pm .010$	-.25 $\pm .20$	9.55 $\pm .21$	-.15 $\pm .10$	9.65 $\pm .11$
1.0	10.332 $\pm .006$	-.064 $\pm .029$	-.675 $\pm .078$	-.184 $\pm .018$	-.33 $\pm .25$	9.45 $\pm .26$	-.37 $\pm .07$	9.40 $\pm .11$
3.0	10.332 $\pm .006$	+.30 $\pm .18$	-.62 $\pm .22$	-.21 $\pm .05$	-.57 $\pm .46$	9.65 $\pm .54$	-.69 $\pm .09$	9.53 $\pm .30$

(logarithm of quantity indicated)						
I	$K_{12}^0$	$\gamma_{H_2CO_3}$	$B_2$	$K_{12}$ <u>interpolated</u>	$B_2$ <u>actual</u>	$K_{12}$
0.1	6.356 $\pm .004$	0 $\pm .01$	+.015 $\pm .009$	6.147 $\pm .016$		
0.5	6.356 $\pm .004$	0 $\pm .02$	+.057 $\pm .030$	6.05 $\pm .05$	+.077 $\pm .030$	6.03 $\pm .05$
1.0	6.356 $\pm .004$	0 $\pm .04$	+.10 $\pm .05$	6.01 $\pm .07$	+.084 $\pm .020$	6.02 $\pm .06$
3.0	6.356 $\pm .004$	0 $\pm .10$	+.27 $\pm .12$	6.18 $\pm .24$	+.22 $\pm .04$	6.23 $\pm .22$

$$B_1 = \frac{1 + K_1'' [Na^+]}{1 + K_1 [Na^+]}$$

$$B_2 = 1 + K_1'' [Na^+]$$

not seem to include any estimate of the systematic error resulting from the Debye-Hückel calculations or activity coefficients, and this hidden source of systematic error can be quite substantial, particularly since the ratio of the ion-pairing contribution to the activity coefficient contribution is not greatly enhanced at low ionic strengths. All of these considerations make plausible the apparent discrepancy between our values and Nakayama's values ( Table XII) for the ion-pairing constants, quite apart from the obviously different nonthermodynamic assumptions used in the two types of calculation.

Garrels, et al.,<sup>30</sup> arrived at values for  $K_1^0$  which are in good agreement with our values, but obtained a higher value for  $K_1^1$ . Again, Garrels was working primarily through the protonation equilibria, and we have seen that discrepancies of 0.3 logarithmic unit can occur simply between different experimental techniques in the same ionic medium. When one adds to this all the complications of correcting to zero ionic strength, the discrepancy of 0.3 to 0.4 logarithmic unit in  $K_1^1$  is not surprising. An additional assumption made by Garrels, which has not been assessed quantitatively, is that the Walker values of carbonate activity coefficients obtained from potassium salts are a reflection of the true activity coefficient values. We have also made this assumption in our correction to zero ionic strength. As we have discussed above, this is one of the main sources of uncertainty. Our current experimental work ( Section II and III of this report ), which will give thermodynamic mean activity coefficients of alkali metal carbonates and bicarbonates, will at least permit a rigorous approach to this problem.

### III. ALKALI METAL CARBONATES

Experiments have been carried out in an attempt to measure accurately the activity coefficients of  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  in aqueous solution. Early work by Walker, Bray and Johnson<sup>27</sup> does not provide these data since their measurements were made using cells with liquid junction. EMF measurements in this work were made using a silver-silver carbonate electrode with either a sodium-glass (Corning no. 476210, glass composition NAS-11-18) or a cationic (Beckman no. 39137, glass composition NAS-27-5) electrode. Silver carbonate was prepared in the following manner, based on the work of Walker, Bray and Johnson. (All solutions were prepared using reagent grade chemicals and triply-distilled water).

Approximately 250 ml of 0.3M  $\text{AgNO}_3$  were placed in a flask and stirred. Slow addition of concentrated  $\text{NH}_4\text{OH}$  caused the clear solution to darken with  $\text{Ag}_2\text{O}$  precipitate. The addition of  $\text{NH}_4\text{OH}$  was continued until the precipitate had just disappeared. The solution of the silver-ammonia complex was filtered, and a slow stream of  $\text{CO}_2$  was passed through it yielding yellow, crystalline  $\text{Ag}_2\text{CO}_3$ .

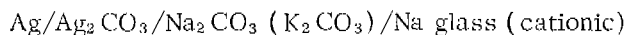
The  $\text{Ag}_2\text{CO}_3$  was analyzed in the following manner. Samples of the salt were vacuum dried at 100 °C and at room temperature. Those which were heated were considerably darkened. A portion of each sample was weighed and dissolved in concentrated nitric acid, and the pH was adjusted to 1.5 to 2.0 with  $\text{NaOH}$ . These " $\text{AgNO}_3$ " solutions were then analyzed for silver by potentiometric titration with standard  $\text{HCl}$ . Under the assumption that all the silver in the samples existed as  $\text{Ag}_2\text{CO}_3$ , the samples tested were found to be 99.7% by weight  $\text{Ag}_2\text{CO}_3$ . These analyses are being repeated more carefully to improve the accuracy. Potential measurements made using the silver-silver carbonate electrodes prepared from this material were stable ( $\pm 0.2$  mV or less, except at concentrations  $< 10^{-5}$  M).

Stock solutions of  $\text{Na}_2\text{CO}_3$  (2 and 0.1M) and  $\text{K}_2\text{CO}_3$  (7 and 0.1M) were prepared and analyzed by potentiometric titration with standard  $\text{HCl}$ . Samples at other concentrations were prepared by weight from these solutions. Solutions of  $\text{NaCl}$  and  $\text{KCl}$  for the reference cells were prepared and analyzed by potentiometric titration with  $\text{AgNO}_3$ .

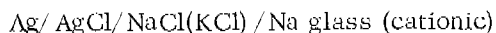
The cells used were of two compartments, separated by a "D" frit, in a U-configuration with a well in one compartment for the  $\text{Ag}_2\text{CO}_3$  electrode. Measurements of potential were made



using the cells:



and



Parentheses are used to indicate the cells for the alternate measurements.

The potential difference between these cells could be compared with results reported by Walker, et al., who measured the potential difference (including liquid junction) between an  $\text{Ag}/\text{Ag}_2\text{CO}_3$  electrode in a  $\text{KHCO}_3$ - $\text{K}_2\text{CO}_3$  solution of known ionic strength and an  $\text{Ag}/\text{AgCl}$  electrode in the identical solution also containing  $\text{KCl}$ .

In each run, the test cells were prepared in the following way. The  $\text{Ag}_2\text{CO}_3$  well was masked to prevent light exposure and an acid-etched silver coil was placed in it.  $\text{Ag}_2\text{CO}_3$  was packed around the coil and glass wool was used to plug the well. The electrode was wetted with the solution of interest and the cell was filled from the opposite compartment. This was done to allow time for equilibrium to be reached and to minimize diffusion of silver ion to the glass electrodes. The complete unit was placed in a water bath ( $25^\circ\text{C}$ ) with the reference cell.

Potentials were measured using a Beckman Research pH meter by transferring the glass electrode (with rinsing) between test and reference cells. The solution in the non-well compartment was then extracted and replaced and the measurement repeated. This procedure was repeated until a constant  $\Delta E$  value was obtained. (Typically, the cells required about 3 hr to equilibrate, and three changes of solution were measured.) The potential differences obtained in this manner are presented in Table XVIII. The pH of solutions was measured independently using a combination pH electrode (Fisher Scientific, no. 13-639-90).

The Nernst equation for these cell reactions can be written:

$$E = E^0 - \frac{RT}{2F} \ln (4m^3 \gamma_{\pm}^3) \quad (42)$$

where

$$E = E_{\text{reference cell}} - E_{\text{test cell}}$$

$$m = \text{molal concentration of } \text{Na}_2\text{CO}_3 \text{ or } \text{K}_2\text{CO}_3$$

$$\gamma_{\pm} = \text{mean activity coefficient of } \text{Na}_2\text{CO}_3 \text{ or } \text{K}_2\text{CO}_3$$

The value for  $E^0$  can be obtained by extrapolation of the cell potentials measured at different electrolyte concentrations to zero concentration. This was done by assuming that  $\log \gamma_{\pm}$  is given by the Davies equation:

$$\log_{10} \gamma_{\pm} = -2 A \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right) \quad (43)$$

Table XVIII. Activity Coefficient Data for  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ 

Salt	Molal Concentration	$\Delta E$ ( $E_{\text{ref}} - E_{\text{test}}$ )	pH	$E^\circ$	$\text{Log } \gamma_{\pm}$ (Davies)	$\text{Log } \gamma_{\pm}$ (Calc.)
$\text{Na}_2\text{CO}_3$	2.0997	0.1073	11.820	0.2029	0.5545	-0.6604
	1.4992	0.1294	—	0.1827	0.2239	-0.7631
	1.0235	0.1368	11.612	0.1535	-0.0230	-0.6808
	0.1001	0.2007	11.376	0.1033	-0.2992	-0.3913
	$1.0035 \times 10^{-2}$	0.2682	10.925	0.0959	-0.1444	-0.1532
	$9.9762 \times 10^{-4}$	0.3561	10.247	0.1030	-0.0522	-0.1413
	$1.0071 \times 10^{-4}$	0.4294	[ 7.425]	0.0910	-0.0173	0.0284
	$4.01 \times 10^{-6}$	0.4795	—	0.0182	-0.0035	0.8637
$\text{K}_2\text{CO}_3$	6.7453	0.0585	13.644	0.4415	3.2872	-0.5631
	3.4663	0.0873	12.663	0.2719	1.3402	-0.5985
	1.0482	0.1295	11.960	0.1482	-0.0107	-0.5548
	0.0984	0.2047	11.502	0.1067	-0.2983	-0.3749
	$1.0033 \times 10^{-2}$	0.2729	11.065	0.1006	-0.1444	-0.1520
	$1.0040 \times 10^{-3}$	0.3529	10.522	0.1000	-0.0524	-0.0539
	$1.0043 \times 10^{-4}$	0.4414	9.435	0.1029	-0.0173	-0.0515
	$9.842 \times 10^{-6}$	0.4829	[ 7.100]	0.0560	-0.0055	0.4895
	$1.005 \times 10^{-6}$	0.4975	—	0.0170	-0.0018	1.3159

where

$$A = 0.509 \text{ at } 25^\circ \text{C}$$

$$z_+ z_- = 2$$

$$I = 3m$$

Using the  $E^0$  value obtained in the above fashion, the activity coefficients for the solutes under consideration can be calculated. Our values for  $E^0$  [0.0951 for  $\text{Na}_2\text{CO}_3$ , 0.0999 for  $\text{K}_2\text{CO}_3$  (see Fig. 7)] are approximate because of the limits of our data. (Further measurements at concentrations between  $10^{-1}$  and  $10^{-2}m$  are being carried out to refine our results.) The above approach was incorporated into a computer program (Table XIX), the results of which appear in Table XVIII. The variance of  $\log \gamma$  with concentration is shown in Fig. 8.

The Davies equation should hold at concentrations between  $10^{-1}$  and  $10^{-4}m$ . At higher concentrations, one would expect deviations as a result of specific ion pairing effects.

From Fig. 9, it is clear that the expected Nernst slope is not observed at low concentrations of carbonate. This deviation can be qualitatively explained by the finite solubility of  $\text{Ag}_2\text{CO}_3$ , which contributes silver ions to the solution, even when there is no excess  $\text{Na}_2\text{CO}_3$  or  $\text{K}_2\text{CO}_3$  present. In more quantitative terms, we may make the following calculations based on the known solubility product<sup>27</sup> of  $\text{Ag}_2\text{CO}_3$ :  $K_{so} = 10^{-11.09}$ .

The potential of the cell:



is given by the Nernst expression:

$$E = E_{\text{CO}_3}^0 - \frac{RT}{2F} \ln [\text{CO}_3^{2-}] - E_{\text{Na}}^0 - \frac{RT}{F} \ln [\text{Na}^+] - \frac{3RT}{2F} \ln \gamma_{\pm} \quad (44)$$

where we have already evaluated

$$E^{0'} = E_{\text{CO}_3}^0 - E_{\text{Na}}^0 = 0.100 \quad (45)$$

in the course of obtaining the mean activity coefficients. At low concentrations, these activity coefficients approach unity, so we may set  $\gamma_{\pm} = 1.0$  for the present argument.

The potential of the Ag electrode may be expressed either as a  $\text{CO}_3$ -reversible or Ag-reversible couple

$$E_{\text{Ag}} = E_{\text{CO}_3}^0 - \frac{RT}{2F} \ln (\text{CO}_3^{2-}) = E_{\text{Ag}}^0 + \frac{RT}{F} \ln [\text{Ag}^+] \quad (46)$$

which leads to the relation

$$E_{\text{Ag}}^0 - E_{\text{CO}_3}^0 = -\frac{RT}{2F} \ln K_{so} = +0.327 \quad (47)$$

and hence to

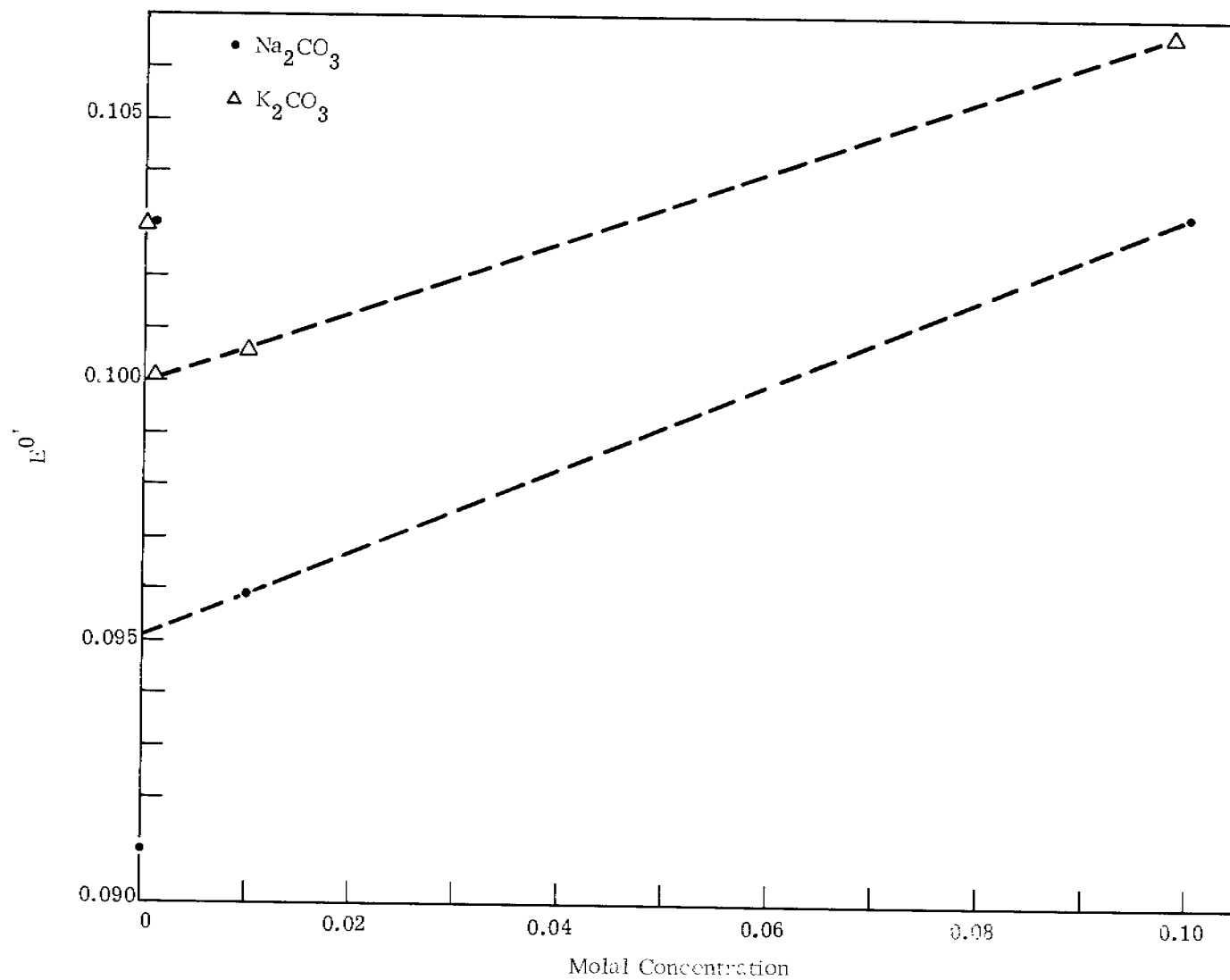


Fig. 7. Extrapolation of  $E^{\circ}$  values to zero concentration to obtain  $E^{\circ}$

Table XIX. Computer Program for Calculating  $E^0$  and  $\log \gamma_{\pm}$

```

1.00 TYPE "      E0 CALCULATIONS
"
1.10 DEMAND N
1.20 DEMAND M(I), DE(I) FOR I = 1 TO N
1.30 LG(I) = -(1.018)*(((SQRT(3*M(I)))/(1+SQRT(3*M(I))))
-(0.2*(3*M(I)))) FOR I = 1 TO N
1.40 A = 1.5*0.05915*LOG10(1.587401)
1.50 B = 1.5*0.05915
1.55 T(I) = LOG10 (M(I)) FOR I = 1 TO N
1.60 E(I) = DE(I) + A + (B*LG(I)) + (B*T(I)) FOR I = 1 TO N
1.61 DEMAND E0
1.62 TO STEP 1.95 IF E0 = 0
1.65 LGC(I) = ((E0-DE(I)-A-(B*T(I)))/B) FOR I = 1 TO N
1.70 TYPE A, B
1.80 TYPE
      MOLAL CONC.      DELTA E      LOG G-D      E0      LOG G-C "
1.90 TYPE IN FORM 1: M(I), DE(I), LG(I), E(I), LGC(I) FOR I=1 TO N
1.91 PAGE
1.92 TO STEP 1.61
1.95 PAGE
1.97 TO STEP 1.10

FORM 1:
      ZZ.ZZZZZZZZ      ZZ.ZZZZ      ZZZ.ZZZZZ      ZZ.ZZZZZ      ZZZ.ZZZZZ

```

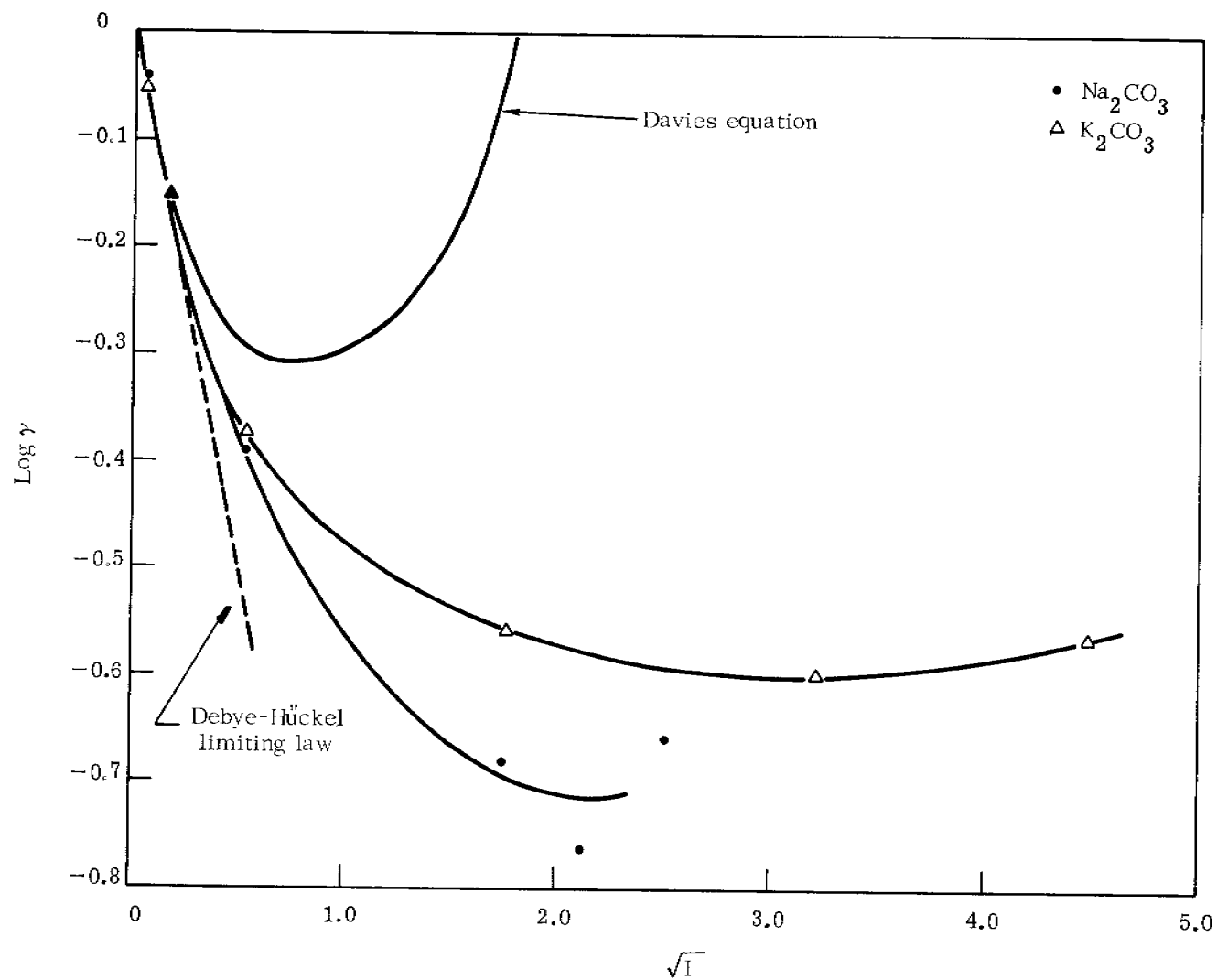


Fig. 8. Experimental and theoretical variance of  $\log \gamma$  with concentration

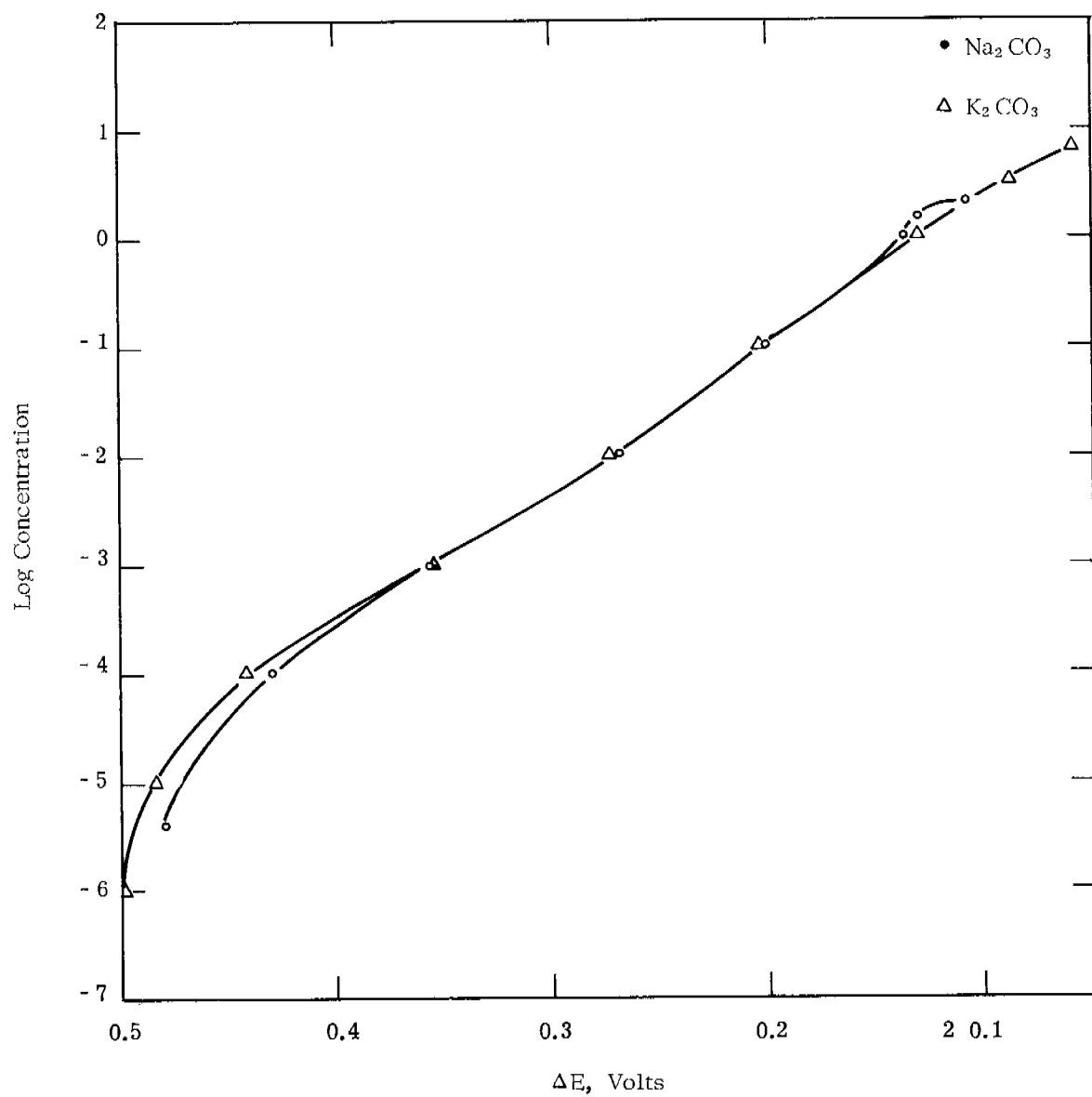


Fig. 9. Deviation of potential from Nernstian behavior as a function of concentration (see text)

$$E = E^0 + \frac{RT}{F} \ln [Ag^+] - \frac{RT}{F} \ln [Na^+] \quad (48)$$

where  $E^0 = 0.427$  and  $[Na^+] = 2m$ .

The silver-ion concentration  $[Ag^+]$  is obtained from the equilibria and mass balances:

$$[Ag^+]^2 [CO_3^{2-}] = K_{so} \quad (49)$$

$$m + \frac{[Ag^+]}{2} = [CO_3^{2-}] + K_1 [H^+] [CO_3^{2-}] \quad (50)$$

where  $K_1 = 10^{10.33}$  is the formation constant of  $HCO_3^-$ .<sup>43</sup> These calculations have been incorporated into the computer program of Table XX.

Two cases must be considered for optimum convergence of the iterations. In the first case, when  $m$  is much less than  $[Ag^+]$  (part 3), then the recursion formula

$$[Ag^+]^3 = 2 K_{so} (1 + K_1 [H^+]) - 2m [Ag^+]^2 \quad (51)$$

converges nicely. In the second case, when  $m$  is much greater than  $[Ag^+]$  (part 4), the recursion formula:

$$[Ag^+]^2 = \frac{K_{so} (1 + K_1 [H^+]) - 1/2 [Ag^+]^3}{m} \quad (52)$$

gives faster convergence. In the program, convergence is assumed to have taken place when two successive value of  $[Ag^+]$  agree to one part in  $10^4$ .

The theoretical values are compared with the experimental values in Table XXI and Fig. 10. The deviations in the concentrated region ( $m > 0.01$ ) are simply due to the activity coefficients of the alkali metal carbonate. In the region from 0.01 to 0.0001, the agreement is good. The deviations at lower values of  $m$  may be attributed to two effects. First, the pH of the solutions was not measured at the same time as the potentials were measured, and may be too acid because of absorption of  $CO_2$  from the atmosphere. This would tend to make the calculated  $E$  values too large. Second, at the very low concentrations, we expect to observe quite large liquid junction potentials ( $\sim 0.1$  V) between the dilute  $Na_2CO_3$  or  $K_2CO_3$  solution in one compartment and the solution saturated with  $Ag_2CO_3$  in the other compartment. These potentials will be particularly large because of the presence of a divalent ion, as well as because of the concentration gradients through the frit.

In conclusion, we can say that we have semiquantitative agreement in the very dilute region, but that the experimental technique would have to be refined before reliable estimates of the effect of liquid junctions could be separated from the effects of pH changes.



Table XX. Computer Program for Comparison of Experimental and Theoretical Potential Values

```

1.10 OPEN "DATA" FOR INPUT AS FILE 1
1.11 READ FROM 1: N
1.12 READ FROM 1: I, E(I), I, PH(I), I, MEX(I) FOR I = 1 TO N
1.13 CLOSE 1
1.20 R(I) = 10^-PH(I) FOR I = 1 TO N
1.30 KSO = 10^-11.09, K1 = 10^-12.33, E0 = 0.427
1.32 KP(I) = KSO*(1+K1*R(I)) FOR I = 1 TO N
1.35 M(I) = MEX(I) FOR I = 1 TO N
1.36 MO(I) = (2*KP(I))^(1/3) FOR I = 1 TO N
1.38 TYPE IN FORM 1:
1.40 DO PART 2 FOR I = 1 TO N

2.1 DO PART 3 IF MO(I) > M(I)
2.2 DO PART 4 IF MO(I) <= M(I)
2.3 AG(I) = AG
2.4 EC(I) = E0 + 0.05915*LOG10(0.5*AG(I)/M(I))
2.5 TYPE IN FORM 2: M(I), PH(I), E(I), EC(I), AG(I), H(I)

3.1 AG = MO(I), AGN = AG
3.2 AG = (2*KP(I) - 2*M(I)*AG^2)^(1/3)
3.3 DONE IF ABS(1-AG/AGN) < 10^-4
3.4 AGN = AG
3.5 TO STEP 3.2

4.1 AG = SQRT(KP(I)/M(I)), AGN = AG
4.2 AG = SQRT((KP(I)-0.5*AG^3)/M(I))
4.3 DONE IF ABS(1-AG/AGN) < 10^-4
4.4 AGN = AG
4.5 TO STEP 4.2

FORM 1:
      M          PH          E          EC          AG          H
FORM 2:
7.7777777777 77.7777 77.7777 77.7777 #####

```

Table XXI. Comparison of Experimental and Theoretical Potential Values

M	PH	E	EC	AG	H
6.7453000000	13.644	0.0585	0.0077	1.098E-06	2.270E-14
3.4663000000	12.663	0.0873	0.0334	1.535E-06	2.173E-13
1.0482000000	11.960	0.1295	0.0797	2.817E-06	1.096E-12
.0984000000	11.502	0.2047	0.1714	9.389E-06	3.148E-12
.0100330000	11.065	0.2729	0.2607	3.095E-05	8.610E-12
.0010040000	10.522	0.3529	0.3529	1.122E-04	3.006E-11
.0001004300	9.435	0.4414	0.4496	4.649E-04	3.673E-10
.0000098420	7.100	0.4829	0.5563	3.016E-03	7.943E-08
.0000012050	7.000	0.4975	0.6169	3.263E-03	1.000E-07

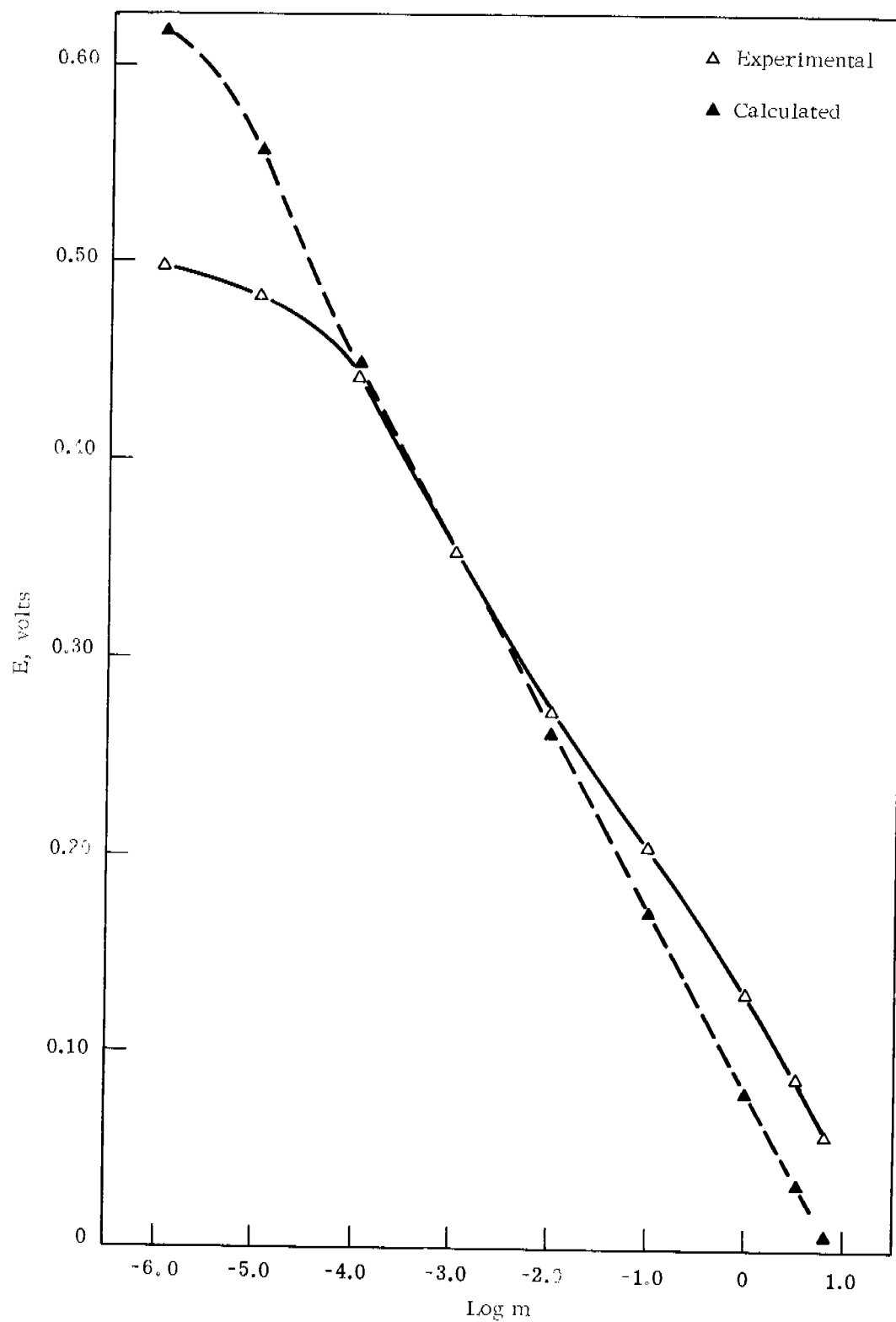


Fig. 10. Comparison of theoretical and experimental values of potential as a function of concentration (see text)

#### IV. Na-Cl-Mg-SO<sub>4</sub> ELECTROLYTES

##### A. Introduction

In attempting to refine the chemical model for multicomponent saline solutions, a study of the activity coefficients of NaCl in four-component mixed electrolytes has been undertaken. These electrolytes contain the ionic components Na<sup>+</sup>, Cl<sup>-</sup>, Mg<sup>2+</sup>, and SO<sub>4</sub><sup>2-</sup>. The experiments are complicated, not only because of the additional component introduced, but because of the possibility of relatively strong ion-pair formation between Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>. Association constants as large as  $K_1 = 10^{2.25}$  have been reported for this pair of ions.<sup>18</sup>

Initially, we explored the possible effect an ion-pairing equilibrium of this magnitude might have on the ionic strength of electrolytes containing both Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>. Because these were not necessarily present in equivalent concentrations, we included the possible effect of other salts (Na<sub>2</sub>SO<sub>4</sub>, MgCl<sub>2</sub>) which could contribute these ions. The concentration of MgSO<sub>4</sub> ion pairs is calculated from the equilibrium. We have:

$$[ \text{Mg}^{2+} ] = m_3 + m_4 - K_1 [ \text{Mg}^{2+} ] [ \text{SO}_4^{2-} ] \quad (53)$$

$$[ \text{SO}_4^{2-} ] = m_2 + m_4 - K_1 [ \text{Mg}^{2+} ] [ \text{SO}_4^{2-} ] \quad (54)$$

where component 1 is NaCl, component 2 is Na<sub>2</sub>SO<sub>4</sub>, component 3 is MgCl<sub>2</sub>, and component 4 is MgSO<sub>4</sub>. The equilibrium constant used contains the activity coefficients of the divalent ions

$$K_1 = 10^{2.25} \gamma_{2+} \gamma_{2-} \quad (55)$$

Now, these activity coefficients are not directly separable from the ion-pairing equilibrium except under conditions (such as in a large excess of noncomplexing electrolyte) which are not directly applicable to our current problem. Thus, the value of  $K_1$  used could critically affect our assumptions about the actual ionic strength of the solutions. This ionic strength is given by

$$I = m_1 + 3 m_2 + 3 m_3 + 4 m_4 - 4 X \quad (56)$$

where  $X$  is the concentration of MgSO<sub>4</sub> ion pairs, which is obtained by solving the quadratic equation

$$K_1 X^2 + BX + C = 0 \quad (57)$$

with

$$B = -K_1 (m_2 + m_3 + 2 m_4) - 1$$

$$C = K_1 (m_3 + m_4) (m_2 + m_4)$$

Using the computer program (MgSO<sub>4</sub>) given in Table XXII, we calculated the concentrations of each salt required to obtain a given final ionic strength with a given set of ratios  $m_2/m_1$ ,  $m_3/m_1$ , and  $m_4/m_1$ . To do this, we made three separate assumptions regarding the value of  $K_1$ : (1) that  $K_1 = 0$  (no ion pairing considered formally), (2) that  $K_1 = 10^{2.25} = 177.8$  for all ionic strengths (no activity coefficient corrections considered formally), and (3) that  $K_1$  was given by Eq. (55), above, with the activity coefficients  $\gamma_{2+} = \gamma_{2-} = \gamma_2$  being calculated by the Davies equation:

$$\log \gamma_2 = -(0.509) (4) \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2 I \right) \quad (58)$$

Admittedly, this is not necessarily a good assumption at high ionic strengths, but it is at least a self-consistent method for calculating approximately the activity coefficient contributions to the ion-pairing equilibrium. It turns out that the form of Eq. (58) makes little difference in the present case.

In order to obtain a self-consistent set of results, it was necessary to make an iterative calculation. Since the ionic strength value was assumed, the activity coefficient  $\gamma_2$  and hence  $K_1$  could be obtained directly. Then, assuming the given ratios of  $m_i$  with  $X = 0$ , Eq. (56) was used to obtain  $m_1$  and hence the individual  $m_i$ . Then Eq. (57) was solved to obtain a value of  $X$ . This was in turn substituted in Eq. (56) and the iteration continued until two successive values of  $m_1$  agreed to 1 part in  $10^7$ . The results of these calculations are reported in Table XXIII. We have distinguished between a nominal (or "true") ionic strength, given by Eq. (56) with  $X$  calculated from Eq. (57), in which ion pairing has been explicitly included, and a formal ionic strength, which is given by Eq. (56) with  $X = 0$ . This latter is usually the way ionic strength is expressed for single salts or simple mixtures.

Even at low ionic strengths, the concentrations of salt required are fairly sensitive to the assumption of ion pairing (i.e.,  $K_1 = 0$  or  $10^{2.25}$ ), but because of compensation in the equations, the activity coefficient values do not make much difference at all in either the final concentrations or in the formal ionic strength (although they make a dramatic difference in  $K_1$ ). This, at least, is fortunate.

Table XXII. Computer Program to Assess Ion-Pairing Effects in Solution  
Containing  $Mg^{2+}$  and  $SO_4^{2-}$

MGS04 JCS 12/3/69

```

1.00 TYPE "IONIC STRENGTH OF MGS04 SOLUTIONS
      1 = NaCl, 2 = Na2SO4, 3 = MgCl2, 4 = MGS04"
1.10 K0 = 10^2.25, X = 0
1.21 DEMAND I
1.22 TYPE "RATIOS TO NaCl"
1.23 DEMAND R2, R3, R4
1.31 LG2 = 2.036*(SQRT(I)/(1+SQRT(I)))-0.2*I
1.32 K1 = K0*10^(-2*LG2)
1.33 DEMAND K1
1.34 TYPE K1
1.35 X = 0 IF K1 = 0
1.41 M1 = (1+4*X)/(1+3*R2+3*R3+4*R4)
1.42 M2 = M1*R2, M3 = M1*R3, M4 = M1*R4
1.43 TO STEP 1.81 IF K1 = 0
1.51 B = -K1*(M2+M3+2*M4)-1
1.52 C = K1*(M3+M4)*(M2+M4)
1.53 DISC = B*B-4*C*K1, B2 = B*B/(400*C*K1)
1.60 X = -(B+SQRT(DISC))/(2*K1) IF B2 < 1
1.61 TO STEP 1.71 IF B2 < 1
1.62 XN = (C+K1*X^2)/(-B)
1.64 TO STEP 1.71 IF ABS(X/XN-1) < 10^-7
1.65 X = XN
1.66 TO STEP 1.62
1.71 MTEST = M1
1.72 DO STEP 1.41
1.73 TO STEP 1.81 IF ABS(MTEST/M1-1) < 10^-7
1.74 TO STEP 1.42
1.81 TYPE M1, M2, M3, M4, X
1.815 IS = M1 + (3*M2) + (3*M3) + (4*M4)
1.816 TYPE IS
1.82 TO STEP 1.21

```

Table XXIII. Results of Calculations

I Nominal	K	Ratio to NaCl			Concentration				X	I Formal
		$R_{Na_2SO_4}$	$R_{MgCl_2}$	$R_{MgSO_4}$	$M_{NaCl}$	$M_{Na_2SO_4}$	$M_{MgCl_2}$	$M_{MgSO_4}$		
0.50	0	1	0	1.5	0.0500	0.0500	0	0.0750	0	0.500
		0.5	0	0.25	0.1429	0.0714	0	0.0357		
		0	0.5	0.25	0.1429	0	0.0714	0.0357		
		0	1	1.5	0.0500	0	0.0500	0.0750		
	177.8	1	0	1.5	0.1174	0.1174	0	0.1761	0.1685	1.174
		0.5	0	0.25	0.1958	0.0979	0	0.0490		
		0	0.5	0.25	0.1958	0	0.0979	0.0490		
		0	1	1.5	0.1174	0	0.1174	0.1761		
	9.34	1	0	1.5	0.0739	0.0739	0	0.1108	0.0597	0.739
		0.5	0	0.25	0.1663	0.0831	0	0.0416		
		0	0.5	0.25	0.1663	0	0.0831	0.0416		
		0	1	1.5	0.0739	0	0.0737	0.1108		
	1.00	1	0	1.5	0.1000	0.1000	0	0.1500	0	1.000
		0.5	0	0.25	0.2857	0.1429	0	0.0714		
		0	0.5	0.25	0.2857	0	0.1429	0.0714		
		0	1	1.5	0.1000	0	0.1000	0.1500		
		1	0	1.5	0.2420	0.2420	0	0.3630		0.3550
		0.5	0	0.25	0.3957	0.1978	0	0.0989		
		0	0.5	0.25	0.3957	0	0.1978	0.0989		
		0	1	1.5	0.2420	0	0.2420	0.3630		
	10.67	1	0	1.5	0.1775	0.1775	0	0.2662	0.1936	1.775
		0.5	0	0.25	0.3555	0.1777	0	0.0889		
		0	0.5	0.25	0.3555	0	0.1777	0.0889		
		0	1	1.5	0.1775	0	0.1775	0.2262		
2.00	0	1	0	1.5	0.2000	0.2000	0	0.3000	0	2.000
		0.5	0	0.25	0.5714	0.2857	0	0.1429		
		0	0.5	0.25	0.5714	0	0.2857	0.1429		
		0	1	1.5	0.2000	0	0.2000	0.3000		

Nominal I given by Eq. (56) with X calculated from Eq. (57).

Formal I given by Eq. (56) with X = 0.

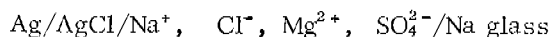
Table XXIII. (Cont.)

I Nominal	K	Ratio to NaCl			Concentration				X	I Formal
		R <sub>Na<sub>2</sub>SO<sub>4</sub></sub>	R <sub>MCl<sub>2</sub></sub>	R <sub>MgSO<sub>4</sub></sub>	M <sub>NaCl</sub>	M <sub>Na<sub>2</sub>SO<sub>4</sub></sub>	M <sub>MgCl<sub>2</sub></sub>	M <sub>MgSO<sub>4</sub></sub>		
4.00	177.8	1	0	1.5	0.4918	0.4918	0	0.7377	0.7295	4.918
		0.5	0	0.25	0.7956	0.3978	0	0.1989	0.1961	2.785
		0	0.5	0.25	0.7956	0	0.3978	0.1989	0.1961	2.785
		0	1	1.5	0.4918	0	0.4918	0.7377	0.7295	4.918
	31.15	1	0	1.5	0.4585	0.4585	0	0.6878	0.6463	4.585
		0.5	0	0.25	0.7771	0.3885	0	0.1943	0.1799	2.720
		0	0.5	0.25	0.7771	0	0.3885	0.1943	0.1799	2.720
		0	1	1.5	0.4585	0	0.4585	0.6878	0.6463	4.585
	0	1	0	1.5	0.4000	0.4000	0	0.6000	0	4.000
		0.5	0	0.25	1.1429	0.5714	0	0.2857		
		0	0.5	0.25	1.1429	0	0.5714	0.2857		
		0	1	1.5	0.4000	0	0.4000	0.6000		
	177.8	1	0	1.5	0.9917	0.9917	0	1.4875	1.4792	9.917
		0.5	0	0.25	1.5955	0.7978	0	0.3989	0.3961	5.584
		0	0.5	0.25	1.5955	0	0.7978	0.3989	0.3961	5.584
		0	1	1.5	0.9917	0	0.9917	1.4875	1.4792	9.917
	620.7	1	0	1.5	0.9976	0.9976	0	1.4964	1.4940	9.976
		0.5	0	0.25	1.5987	0.7994	0	0.3997	0.3989	5.596
		0	0.5	0.25	1.5987	0	0.7994	0.3997	0.3989	5.596
		0	1	1.5	0.9976	0	0.9976	1.4964	1.4940	9.976
6.00	0	1	0	1.5	0.6000	0.6000	0	0.9000	0	6.000
		0.5	0	0.25	1.7143	0.8571	0	0.4286		
		0	0.5	0.25	1.7143	0	0.8571	0.4286		
		0	1	1.5	0.6000	0	0.6000	0.9000		
	177.8	1	0	1.5	1.4961	1.4916	0	2.2375	2.2291	14.916
		0.5	0	0.25	2.3955	1.1978	0	0.5989	0.5961	8.384
		0	0.5	0.25	2.3955	0	1.1978	0.5989	0.5961	8.384
		0	1	1.5	1.4916	0	1.4916	2.2375	2.2291	14.916
	17573	1	0	1.5	1.4999	1.4999	0	2.2499	2.2498	14.999
		0.5	0	0.25	2.4000	1.2000	0	0.6000	0.6000	8.400
		0	0.5	0.25	2.4000	0	1.2000	0.6000	0.6000	8.400
		0	1	1.5	1.4999	0	1.4999	2.2499	2.2498	14.999

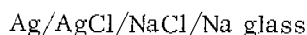
### B. Experimental

Solutions were prepared from reagent grade chemicals and triply-distilled water. They were then analyzed for chloride by potentiometric titration with  $\text{AgNO}_3$ , and for sulfate by the  $\text{BaSO}_4$  gravimetric method (concentrations are given in Table XXIV). For ionic strengths from 0.5 to 2, solutions were prepared by weight from analyzed stock solutions of the four salts. The remaining solutions were prepared by weight and analyzed individually for chloride and sulfate. Using these data and the charge balance equation (see Fig. 11), the concentrations of salts at ionic strengths 4 and 6 were established.

EMF measurements were made of the cell



with a reference cell



The Ag/AgCl electrodes were matched to within 0.1 mV, and the sodium-glass electrode (Corning NAS-11-18) was passed, with rinsing, between the test and reference solutions for measurement. The cells were thermostated at  $25.0 \pm 0.1^\circ\text{C}$  in a water bath. The potentials measured in this way are reported as  $E_{\text{ref}} - E_{\text{test}}$  in Table XXIV.

### C. Results

The activity coefficients for pure NaCl reference solution at each ionic strength were interpolated from the tables of Robinson and Stokes, and the activity coefficients of NaCl in the mixed electrolytes were calculated using the computer program given in Table XXV. Values so obtained are reported in Table XXVI, and plotted as a function of ionic strength in Fig. 12. Because of the monotonic nature of these curves, experimental point 2A is believed to reflect an error in the measurement of  $\Delta E$ .

The next phase in our research on the chemical model for multicomponent electrolytes is theoretical. Although this portion of the work is not complete at the time of writing, the general procedures have been established and will be outlined here.

First, we must establish values of the ion-pairing constants for the strongly associated ions in the Na-Cl-Mg-SO<sub>4</sub> electrolytes. This will be done by using the same type of assumptions we have used in our work on the carbonate systems, which we have already described in Section II. The computer program XPYT can be used with only minor modifications. Assuming that NaCl is nonassociated, we can attribute variations in the mean activity coefficient of NaCl when Na<sub>2</sub>SO<sub>4</sub> is added at constant ionic strength to the formation of the ion pair, NaSO<sub>4</sub><sup>-</sup>. This calculation has been carried out approximately by Pytkowicz and Kester,<sup>25</sup> but it would be necessary for our purposes to make use of the most recent and accurate activity coefficient data<sup>15, 16</sup> in establishing these ion-pairing constants and investigating how well the chemical model fits this particular system.



Table XXIV. Solution Concentrations and Experimental Results

Sample	Weight/100 gms H <sub>2</sub> O				Molal Concentration				Formal I	$\Delta E$ , mV
	NaCl	Na <sub>2</sub> SO <sub>4</sub>	MgCl <sub>2</sub>	MgSO <sub>4</sub>	NaCl	Na <sub>2</sub> SO <sub>4</sub>	MgCl <sub>2</sub>	MgSO <sub>4</sub>		
.5A	0.2927	0.7021	—	0.8989	0.0501	0.0494	—	0.0747	0.4971	87.2
.5B	0.8304	1.0099	—	0.4299	0.1421	0.0711	—	0.0357	0.4982	44.6
.5C	0.8181	—	0.6716	0.4253	0.1400	—	0.0705	0.0353	0.4927	43.6
.5D	0.2878	—	0.4711	0.8887	0.0492	—	0.0495	0.0738	0.4929	86.1
1A	0.5378	1.3941	—	1.7746	0.0982	0.0982	—	0.1474	0.9824	92.0
1B	1.6549	2.0111	—	0.8539	0.2832	0.1416	—	0.0709	0.9916	48.6
1C	1.6294	—	1.3280	0.8391	0.2788	—	0.1395	0.0697	0.9761	46.1
1D	0.5673	—	0.9245	1.7543	0.0971	—	0.0971	0.1457	0.9712	90.0
2A	1.1715	2.8478	—	3.6185	0.2004	0.2005	—	0.3006	2.0043	81.2
2B	3.2789	3.9881	—	1.6892	0.5610	0.2808	—	0.1403	1.9646	40.0
2C	3.1817	—	2.5926	1.6425	0.5444	—	0.2723	0.1365	1.9073	35.7
2D	1.1016	—	1.7940	3.4043	0.1885	—	0.1884	0.2828	1.8849	80.5
4A	2.1852	5.2256	—	6.6360	0.3739	0.3679	—	0.5513	3.6828	111.4
4B	6.4073	7.8423	—	3.3180	1.0963	0.5521	—	0.2756	3.8550	64.8
4C	6.0869	—	5.0428	3.1425	1.0415	—	0.5296	0.2612	3.6751	57.9
4D	2.0899	—	3.3761	6.4403	0.3576	—	0.3546	0.5350	3.5614	105.6
6A	3.1166	7.5661	—	9.6680	0.5333	0.5327	—	0.8032	5.3442	116.4
6B	9.4388	11.4126	—	4.8313	1.6151	0.8035	—	0.4014	5.6312	66.3
6C	8.6934	—	6.6230	4.4804	1.4875	—	0.6956	0.3722	5.0631	59.0
6D	2.9695	—	4.8603	9.2111	0.5081	—	0.5104	0.7652	5.1001	108.4

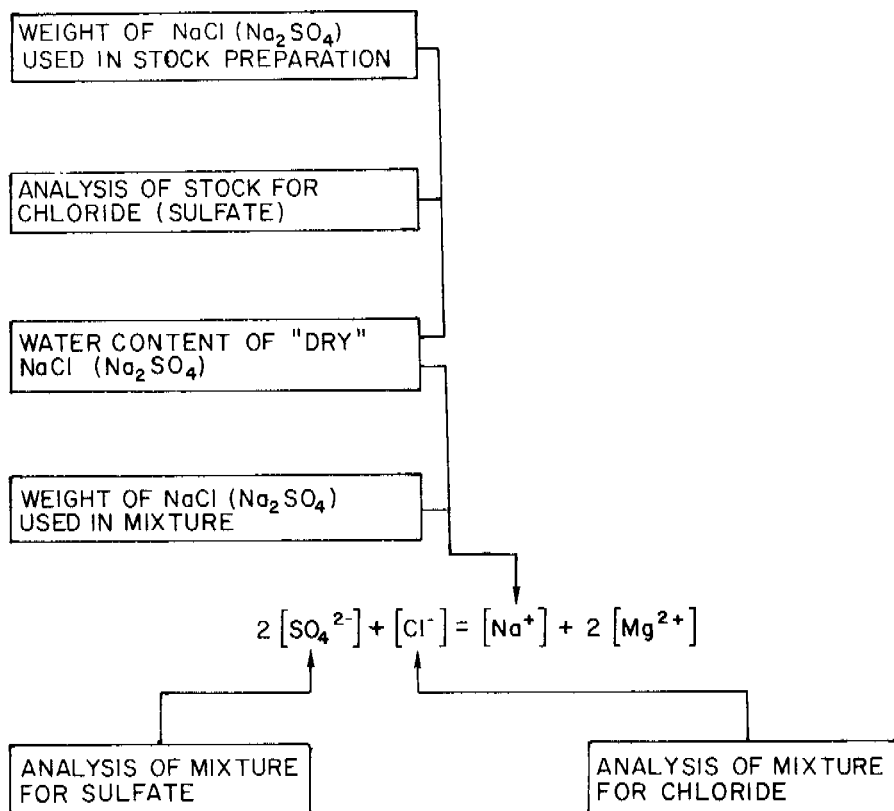


Fig. 11. Method of determining concentration using charge-balance equation

Table XXV. Computer Program for Calculating Log Gamma

COMPUTER PROGRAM FOR CALCULATING LOG GAMMA

PAGE 1

>LOAD  
FROM /LG1/

>TYPE ALL

```

1.00 TYPE "
      CALCULATIONS FOR LOG GAMMA"
1.10 DEMAND MR, REF
1.20 EOR = -118.3*(LOG10 (MR) + (REF-1))
1.30 TYPE EOR
1.50 DO PART 2 FOR J = 1 TO 4
1.60 LINE
1.70 TO STEP 1.10

2.10 DEMAND M1, M2, M3, M4, DE
2.20 MNA = M1+2*M2, MCL = M1+2*M3
2.30 LG = ((-DE-EOR)/118.30)-(0.5*LOG10 (MNA*MCL))
2.40 I = M1+3*M2+3*M3+4*M4
2.50 BAL = 2*(M2+M4)+MCL-MNA-2*(M3+M4)
2.55 TYPE IN FORM 1:
2.60 TYPE IN FORM 2: DE, MNA, MCL, LG, I, BAL
2.70 LINE

```

```

FORM 1:
      DE      MNA      MCL      LG      I      BAL
FORM 2:
      ZZ.ZZ.Z  ZZ.ZZZZ  ZZ.ZZZZ  ZZ.ZZZZ  ZZ.ZZZZ  ZZ.ZZZZ

```

>PAGE

Table XXVI. Activity Coefficients of NaCl in Mixed Electrolytes

Sample	I	$-\log \gamma$	Sample	I	$-\log \gamma$
.5A	0.4971	0.1670	2C	1.9073	0.1664
.5B	0.4982	0.1737	2D	1.8849	0.1724
.5C	0.4927	0.1595	4A	3.6828	0.2370
.5D	0.4929	0.1528	4B	3.8550	0.2253
1A	0.9824	0.1901	4C	3.6751	0.1458
1B	0.9916	0.1952	4D	3.5614	0.1697
1C	0.9761	0.1673	6A	5.3442	0.2518
1D	0.9712	0.1683	6B	5.6312	0.2211
2A	2.0043	0.2051	6C	5.0631	0.1170
2B	1.9646	0.2159	6D	5.1001	0.1640

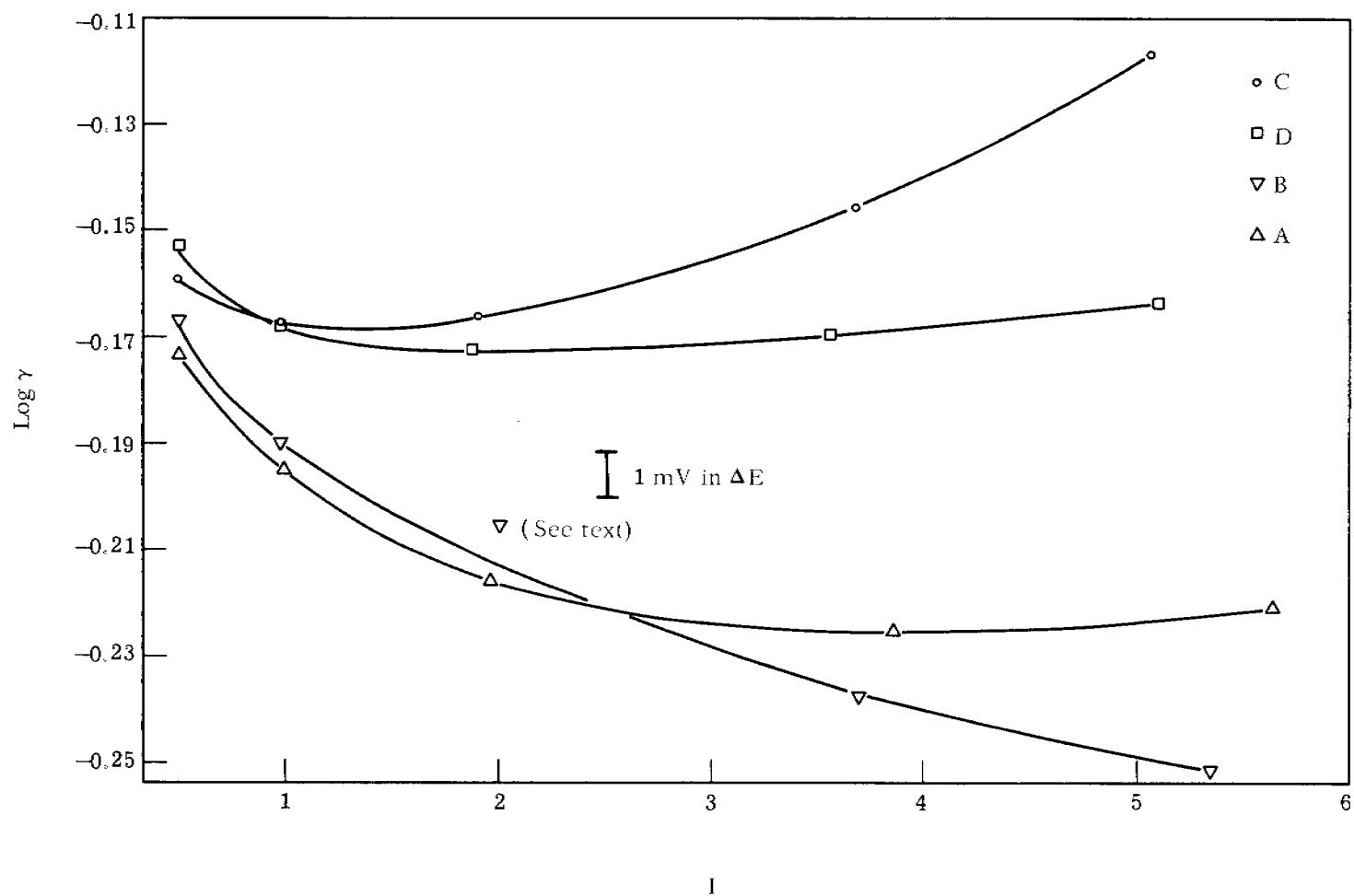


Fig. 12. Mean activity coefficients of NaCl in mixed electrolyte (see Table XXV)

A similar type of calculation can be carried out for the system  $\text{NaCl-MgCl}_2$ .

Because of the small values of the Harned rule coefficients for this system, we expect that the formation constant obtained for  $\text{MgCl}^-$  will be quite small, and that this ion pair can be neglected in further calculations. Nevertheless, it is still of interest to establish quantitatively how accurate such an assumption represents the experimental data.

Having established the extent, if any, to which  $\text{MgCl}^-$  ion pairs are formed, we can then make use of the activity coefficient data for the system  $\text{MgCl}_2\text{-MgSO}_4$  to establish the formation constant for the ion pair,  $\text{MgSO}_4$ . In this calculation, as  $\text{MgSO}_4$  is added at constant ionic strength, we attribute changes in the mean activity coefficient of  $\text{MgCl}_2$  primarily to the formation of the ion pair,  $\text{MgSO}_4$ . We have already made some calculations (summarized earlier in this section) using the ion-pairing constant extrapolated to zero ionic strength as obtained by Nair and Nancollas,<sup>48</sup> but we found in doing these calculations that the ionic strength dependence at high ionic strengths could not be predicted with any useful certainty.

Finally, when all the ion-pairing constants have been established, we can then examine how well the chemical model fits the experimental results. Both our experimental measurements of the mean activity coefficient of  $\text{NaCl}$  (given above) and the values in the literature for the system  $\text{NaCl-MgSO}_4$ <sup>15, 16, 49</sup> can be directly compared with values for the mean activity coefficient of  $\text{NaCl}$  calculated from the chemical model. Again, these calculations will be carried out according to the same algorithms used in the carbonate work (Section II), but of course will be much more complicated because of the possibility of forming three ion-pair species instead of only one.

We believe that extension of the chemical model to high concentrations in systems related to sea water will provide an essential link in the difficult problem of making multicomponent thermodynamic data available for engineering design.

## V. NaCl-NaF ELECTROLYTES\*

### A. Introduction

The activity coefficients of fluoride salts in multicomponent solutions (particularly those containing NaCl) are of considerable interest in connection with the fluoride chemistry of natural waters, and the availability of a highly selective fluoride-reversible electrode<sup>50</sup> has made possible the direct measurement of these thermodynamic quantities. Earlier work with this electrode has been reviewed, and some preliminary experimental values have been reported.<sup>51</sup> We report here experiments with the following cells:

Ag/AgCl/Na<sup>+</sup>, Cl<sup>-</sup>, F<sup>-</sup>, H<sub>2</sub>O/Na(Hg)

Ag/AgCl/Na<sup>+</sup>, Cl<sup>-</sup>, F<sup>-</sup>, H<sub>2</sub>O/Na glass (NAS 11-18)

Na glass/Na<sup>+</sup>, Cl<sup>-</sup>, F<sup>-</sup>, H<sub>2</sub>O/LaF<sub>3</sub> membrane

Ag/AgCl/Na<sup>+</sup>, Cl<sup>-</sup>, F<sup>-</sup>, H<sub>2</sub>O/LaF<sub>3</sub> membrane

The first two cells yield the mean activity coefficient ( $\gamma_{12}$ ) of NaCl in the mixed electrolyte, the third yields the mean activity coefficient of NaF ( $\gamma_{21}$ ), and the fourth yields the ratio  $\gamma_{12}/\gamma_{21}$ . The measurements with the fourth cell are of interest only because they can be made more precisely than can measurements with the second or third cells.

### B. Experimental

The sodium amalgam-silver chloride cell was the same as has been described previously.<sup>1, 32</sup> Experiments with the sodium-selective glass electrode were carried out as previously reported,<sup>33, 52</sup> and the AgCl-LaF<sub>3</sub> cell was exactly the same configuration. For the Na glass-LaF<sub>3</sub> cell, the LaF<sub>3</sub> electrode was connected to the reference electrode input (grounded) of the pH meter, since it has a lower impedance than the glass electrode. The sodium-selective glass electrode<sup>33</sup> was a Corning no. 476210 (glass composition, NAS 11-18) or a Beckman no. 39278 (glass composition, LAS 10-23), and the lanthanum fluoride electrode was an Orion Research model 94-09 with black plastic body. The stability and response time of this later version of the LaF<sub>3</sub> electrode have been improved over earlier versions by a better seal between the crystal and the body.<sup>51</sup>

Solutions were prepared by weight from reagent grade chemicals and triply-distilled water. NaCl (Fisher Certified) contained less than 0.01% bromide, less than 0.002% iodide,

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\*Part of this work has been accepted for publication in *Analytical Chemistry*, September 1970.

and less than 0.0002% materials reducible by sodium amalgam. NaF (BDH reagent 92-584) contained less than 0.002% chloride, less than 0.004% heavy metals, and approximately 0.01% potassium. Stock solutions of NaCl were analyzed by potentiometric titration with standard AgNO<sub>3</sub> using a silver indicator electrode, and stock solutions of NaF were analyzed by titration with standard La(NO<sub>3</sub>)<sub>3</sub> using the LaF<sub>3</sub> electrode as indicator.<sup>5,3</sup> For the amalgam electrode measurements, 0.001m NaOH was added to the stock solutions to minimize hydrogen evolution. The pH of each mixed solution was measured separately, and was never high enough to cause OH<sup>-</sup> interference with the LaF<sub>3</sub> electrode.<sup>50,51</sup>

### C. Results

Consider first the measurements made with the cell

Ag/AgCl/Na<sup>+</sup>, Cl<sup>-</sup>, F<sup>-</sup>, H<sub>2</sub>O/LaF<sub>3</sub> membrane

which gives the ratio of the mean activity coefficients  $\gamma_{12}/\gamma_{21}$ . This cell, although it does not give as direct an approach to the activity coefficients of the individual components, gave data which were more precise than any of our other measurements on the NaCl-NaF system.

By combining measurements of this cell with osmotic coefficients, it is possible to obtain the mean activity coefficients  $\gamma_{12}$  and  $\gamma_{21}$  separately. The potential of this cell is given (IUPAC Stockholm convention) by

$$E = E^\circ + \frac{RT}{F} \ln \left( \frac{m_1}{m_2} \right) + \frac{2RT}{F} \ln \left( \frac{\gamma_{12}}{\gamma_{21}} \right) \quad (59)$$

where  $m_1$  and  $m_2$  are the molal concentrations of NaCl and NaF in the mixed electrolyte, respectively. To eliminate long term uncertainties in  $E^\circ$ , the test solutions were compared with a calibration solution with  $m_{Cl} \approx m_F$ :

$$E^\circ = E_{ref} - \frac{RT}{F} \ln \left( \frac{m_{Cl}}{m_F} \right)_{ref} - \frac{2RT}{F} \ln \left( \frac{\gamma_{12}}{\gamma_{21}} \right)_{ref} \quad (60)$$

To apply Harned's rule, solutions of a given set were approximately the same ionic strength (e.g., 0.5 or 1.0m). Since the concentrations of chloride and fluoride in both the test and reference solutions and the temperature are known, the difference in potential  $\Delta E$  ( $E - E_{ref}$ ) between these solutions gives directly the quantity

$$R_{21} = \log \frac{\gamma_{21}^r \gamma_{12}^t}{\gamma_{12}^r \gamma_{21}^t} \quad (61)$$

where superscript r stands for the reference solution and t stands for the test solution. Experimental values of  $\Delta E$  and  $R_{21}$  are presented in Table XXVII.



Table XXVII. Measurements With the Cell Ag/AgCl/NaCl, NaF, H<sub>2</sub>O/LaF<sub>3</sub> Membrane

I	X <sub>2</sub>	pH	ΔE	R <sub>21</sub>	Q	α <sub>12</sub>	α <sub>12</sub>
0.4929	0.9099	9.33	-57.5	0.0095	-0.0610	-0.0181	-0.0790
0.4934	0.8469	9.59	-41.9	0.0102	-0.0614	-0.0315	-0.0925
0.5226	0.6001	7.90	-5.7	0.0050	-0.0605	-0.0200	-0.1033
0.4965	0.5081	10.31	0	0	—	—	—
0.5421	0.3450	7.73	+20.9	0.0021	-0.0602	+0.0546	-0.0056
0.5629	0.0729	7.41	+69.8	0.0025	-0.0608	+0.0406	-0.0203
0.6239	0.9435	7.31	-69.5	0.0117	-0.0592	0.0078	-0.0514
0.6172	0.8593	7.23	-45.3	0.0016	-0.0592	0.0333	-0.0258
0.6079	0.7442	7.19	-28.2	0.0186	-0.0594	0.0961	-0.0367
0.5894	0.5138	7.01	0	0	—	—	—
0.5635	0.1917	6.71	+38.7	0.0023	-0.0607	0.0367	-0.0240
0.5527	0.0570	6.47	+73.4	-0.0009	-0.0602	0.0284	-0.0318
0.9957	0.9593	7.67	-77.9	-0.0023	-0.0554	0.0303	-0.0251
1.0003	0.8853	7.69	-49.0	-0.0041	-0.0555	0.0335	-0.0220
1.0008	0.8765	7.73	-47.8	0.0039	-0.0555	0.0221	-0.0334
1.0085	0.7537	7.89	-25.9	0.0018	-0.0554	0.0236	-0.0318
1.0225	0.5294	8.01	0	0	—	—	—
1.0409	0.2328	8.19	+33.5	0.0011	-0.0551	0.0299	-0.0253
1.0494	0.0966	7.60	+60.1	0.0030	-0.0551	0.0308	-0.0243

If Harned's rule is assumed to be obeyed for both components, then

$$\log \gamma_{12} = \log \gamma_{10} - \alpha_{12} X_2 I \quad (62)$$

$$\log \gamma_{21} = \log \gamma_{20} - \alpha_{21} X_1 I \quad (63)$$

where  $\gamma_{10}$  and  $\gamma_{20}$  are the activity coefficients of NaCl and NaF, respectively, in solutions containing only that salt at ionic strength,  $I$ , which is the same as the mixed solution. If the ionic strength fraction of NaF,  $X_2$ , is defined by

$$X_2 = 1 - X_1 = \frac{m_F}{m_F + m_{Cl}} \quad (64)$$

one obtains from Eqs. (61) through (64)

$$R_{21} = (\alpha_{12} + \alpha_{21}) (X_{ref} - X_2) \quad (65)$$

where  $X_{ref} = X_2$  in the reference solution.

Independently, from the Gibbs-Duhem relation, one may obtain the relation

$$\alpha_{21} - \alpha_{12} = \frac{2}{2.303 I} (\phi_2^0 - \phi_1^0) = Q \quad (66)$$

where  $\phi_2^0$  and  $\phi_1^0$  are the osmotic coefficients of solutions containing only NaF and NaCl, respectively, at ionic strength  $I$ . Combining this with Eq. (65), we obtain expressions for the two Harned rule coefficients:

$$\alpha_{12} = \frac{R_{21}}{2 I (X_{ref} - X_2)} - \frac{Q}{2} \quad (67)$$

$$\alpha_{21} = \frac{R_{21}}{2 I (X_{ref} - X_2)} + \frac{Q}{2} \quad (68)$$

Thus, from each experimental point in Table XXVII, one can obtain directly a value of  $\alpha_{12}$  and a value of  $\alpha_{21}$ . From osmotic coefficient values listed by Robinson and Stokes,<sup>12</sup> we obtained  $Q$ 's corresponding to different  $I$ 's, and these are listed in Table XXVII along with the resulting Harned rule coefficients. The mean values of these, together with their statistical 95% confidence limits, are presented in Table XXVIII.

Although the other cells give a more direct measurement of the activity coefficients of NaCl or NaF, the results were not only less precise, but seemed to be subject to large systematic errors. Results obtained at ionic strength 1.0 are shown in Figs. 13 and 14. On each figure, a line corresponding to Harned's rule with the coefficients obtained from the data in Table XXVII has been drawn for comparison. Harned rule coefficients evaluated from each data set are

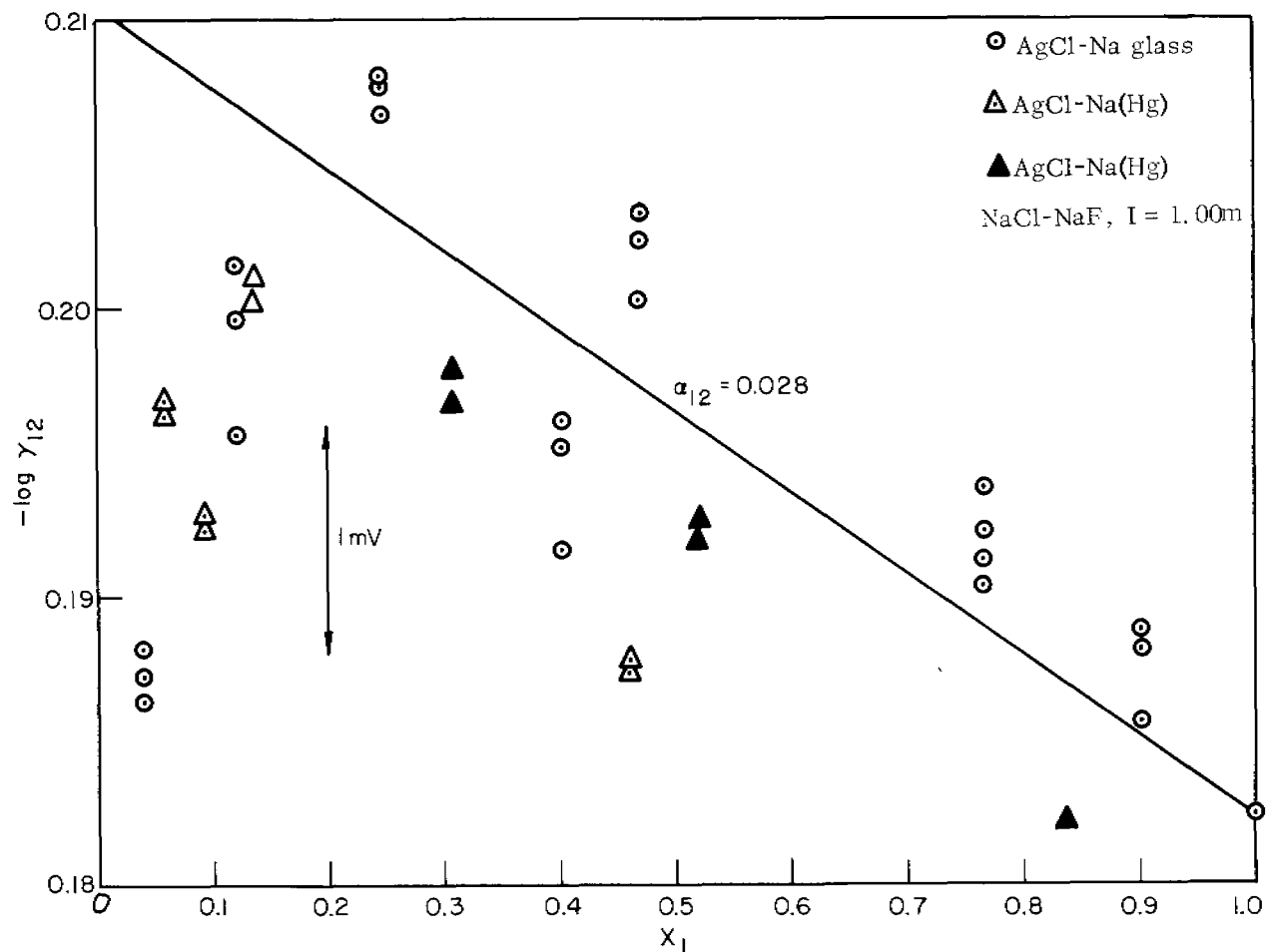


Fig. 13. Direct measurement of the activity coefficients of NaCl in NaCl-NaF electrolytes at ionic strength 1.0m. Note that the two separate series of measurements with the sodium amalgam electrode are in good agreement. The slope of the Harned rule is obtained from the data in Table XXVII

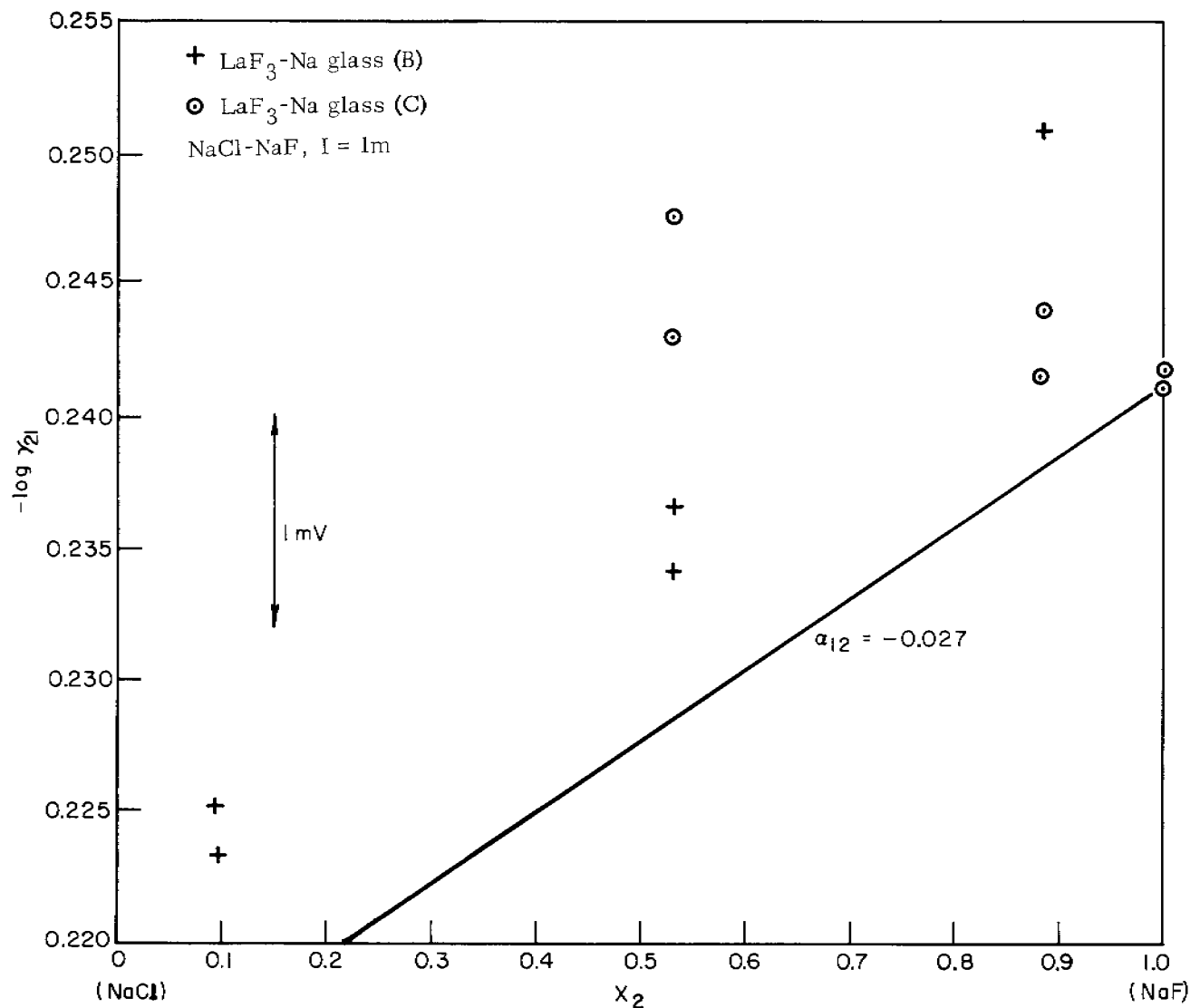


Fig. 14. Direct measurement of the activity coefficient of NaF in NaCl-NaF electrolytes at ionic strength 1.0m. The slope of the Harned rule line is obtained from the data in Table XXVII

listed separately in Table XXVIII, and detailed numerical values have been made available elsewhere.<sup>2</sup>

Table XXVIII. Harned Rule Coefficients for NaCl in Aqueous NaCl-NaF Electrolytes at 25 °C\*

Cell	Na Sensor†	I	pH	$\alpha_{12}$	$\alpha_{21}$
AgCl-LaF <sub>3</sub>	—	0.5 to 0.6	6.5 to 9.5	+0.029 ± 0.014	-0.035 ± 0.015
		1.0	7.6 to 8.2	+0.028 ± 0.002	-0.027 ± 0.002
AgCl-Na	Na(Hg)	0.5	9.3 to 11.0	-0.01 ± 0.03	—
		1.0	10.3 to 11.1	+0.028 ± 0.007	—
	Glass C	0.5	6.4 to 7.3	+0.11 to 0.01	—
		1.0	7.6 to 8.2	+0.01 ± 0.01	—
	Glass C'	0.5	6.4 to 10.3	+0.002 ± 0.016	—
		1.0	7.6 to 8.2	—	+0.005 ± 0.005
LaF <sub>3</sub> -Na	Glass C	1.0	7.6 to 8.2	—	+0.005 ± 0.005
	Glass B	1.0	7.6 to 8.2	—	-0.03 ± 0.01

\*Errors are statistical 95% confidence limits.

†Glass compositions were NAS 11-18 aged 1 yr (C) or new (C') and LAS 10-23 (B).

#### D. Discussion

At ionic strength 1.0, direct measurements of  $\alpha_{12}$  with the AgCl-Na(Hg) cell and direct measurements of  $\alpha_{21}$  with the LaF<sub>3</sub>-glass (B) cell are in good agreement with the values obtained from Table XXVII. Data obtained with the aged glass electrode (C), although relatively self-consistent, did not agree at all with the other measurements. At ionic strength 0.5, data obtained by all methods are much less precise, but are in general agreement with each other, with the exception again of glass electrode C.

In view of these results, we recommend the following "best values" of Harned rule coefficients for calculating the activity coefficients of NaCl or NaF in mixed electrolytes:

$$\alpha_{12} = +0.028 \pm 0.002$$

$$\alpha_{21} = -0.027 \pm 0.002$$

Since the dependence of the experimentally determined Harned rule coefficients on ionic strength (in the range of 0.5 to 1.0) is smaller than the estimated experimental error at I = 0.5, and since the exact values of the Harned rule coefficients have relatively little effect on calculated values of  $\gamma_{12}$  or  $\gamma_{21}$  at lower ionic strengths, the above values of  $\alpha_{12}$  and  $\alpha_{21}$  can be taken to be independent of ionic strength. This assumption probably introduces an error of less than 0.002 in log  $\gamma$ .

The Brønsted theory<sup>13</sup> of ionic interactions, in which the activity coefficient of a given ion is influenced only by the presence of ions of the opposite charge, predicts that  $\alpha_{12} = -\alpha_{21}$ . This is equivalent to the "ideal mixture" of "nonideal solutions" for which the excess free

energy of mixing, and hence the term  $\beta^0$ , is zero. A number of systems involving univalent ions correspond fairly closely to this relatively simple model, and the NaCl-NaF system appears to be one. Others (with values of  $\alpha_{12} + \alpha_{21}$  at  $I = 1.0$  in parentheses) are NaCl-NaBr ( $-0.0017$ ),<sup>5 4</sup> KCl-KBr ( $-0.0011$ )<sup>5 4</sup> or ( $0.000$ ),<sup>5 5</sup> NaCl-KBr ( $+0.0011$ ),<sup>5 4</sup> NaCl-NaNO<sub>3</sub> ( $0.0000$ )<sup>14</sup> or ( $+0.0005$ ),<sup>7</sup> and NaClO<sub>4</sub>-LiClO<sub>4</sub> ( $+0.0015$ ).<sup>5 6</sup> Most other aqueous solutions of two salts show values of this quantity<sup>7</sup> which are greater than  $0.01$  ( $\beta^0 > 0.023$ ), with the exception of the recently studied<sup>1 6</sup> mixtures NaCl-MgSO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>-MgCl<sub>2</sub>, for which  $\beta^0$  is  $-0.007$  and  $-0.006$ , respectively, at  $I = 1$ .

An alternative viewpoint, which might be termed the ion-pairing or chemical model approach,<sup>2 5, 5 7</sup> assumes that all deviations of the activity of a reference salt (e.g., NaCl), from its activity in a solution containing only that salt at the same ionic strength, are due to interactions with other salts in the solution (e.g., NaF). This model predicts a dependence of experimentally measured  $\gamma_{12}$  values of composition which corresponds very closely to Harned's rule with a positive  $\alpha_{12}$ , if there is weak ion pairing of either Na<sup>+</sup> or Cl<sup>-</sup> with an ion of the other salts. Qualitatively, it is apparent from the positive sign for  $\alpha_{12}$  and the negative sign for  $\alpha_{21}$  that the Na<sup>+</sup>-F<sup>-</sup> interactions are substantially stronger than the Na<sup>+</sup>-Cl<sup>-</sup> interactions. Quantitatively, we can calculate, from  $\alpha_{12}$  given above, an equilibrium constant for the formation of the Na<sup>+</sup>-F<sup>-</sup> ion pair by the method previously described:<sup>5 7</sup>

$$\log K_1 = 0.79 \pm 0.04$$

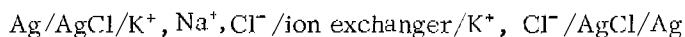
Of course, this value is referred to a standard state in a 1m NaCl medium, not to infinite dilution.

## VI. POTASSIUM-SELECTIVE LIQUID ION-EXCHANGE ELECTRODE\*

### A. Introduction

The availability of a new liquid ion-exchange electrode system which has been reported to be highly selective for potassium over sodium<sup>58, 59</sup> has encouraged us to study its thermodynamic behavior under conditions where quantitative measurements can be made rigorously.<sup>34, 60</sup>

The cell



was measured at 25 °C over a wide range of compositions for the test (left-hand) solution. The reference electrolyte (right-hand compartment) was 0.01M KCl saturated with AgCl and was held constant in composition throughout the measurements. The ion exchanger, obtained from Orion Research, Inc. (Type 92-19) through the courtesy of Drs. M. S. Frant and J. W. Ross Jr., consists of the polypeptide valinomycin in an aromatic solvent.<sup>61</sup> Such an electrode represents a dramatic advance over the presently available potassium-selective glass electrodes (NAS 27-5). Typical glass electrodes have a selectivity of 5:1 for potassium over sodium, whereas the valinomycin system shows a selectivity greater than 1000:1. A number of antibiotics, including valinomycin, the macrolide actins, and the enniatins, have the ability to affect strongly the potassium ion transport in mitochondria.<sup>62</sup> Simon and coworkers<sup>63</sup> reported that the actin homologs dissolved in CCl<sub>4</sub> or benzene could be used to make electrodes which were selective for potassium over sodium. The observed slopes were, however, less than the theoretical (59 mV) Nernst slopes. Later, they reported that a suspension of nonactin in Nujol-octanol gave approximately theoretical slopes between 0.1 and 0.001M K<sup>+</sup>, with a selectivity of 100:1 over sodium. In May 1969, at the New York Meeting of the Electrochemical Society, Simon reported that valinomycin gave a selectivity of 5000:1 over sodium and a "linear response" between 0.1 and 10<sup>-5</sup> M.

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\* Part of this work has been published as Activity Measurements Using a Potassium-Selective Liquid Ion-Exchange Electrode, by J. N. Butler and R. Huston, *Anal. Chem.*, **42**, 676 (1970).

Frant and Ross used 5 to 10% of commercial valinomycin in a variety of aromatic solvents (nitrobenzene and its homologs, diphenyl ether, chlorobenzene, and bromobenzene) as the liquid ion exchanger in the conventional liquid membrane electrode structure. They experienced problems with potassium contamination from KCl salt bridge and were forced to use an additional salt bridge (5M lithium trichloroacetate). We have used a similar system with the same ion exchanger. However, we have used an Ag/AgCl reference electrode in the same solution to avoid variations of the liquid junction potential which results from using a salt bridge and a saturated calomel electrode.

## B. Experimental

Potentials were measured using a Beckman Research pH meter with a digital voltmeter (Tyco DVM-404) as a readout device. Calibration of this system versus an NBS-calibrated standard cell using a Leeds and Northrup model K-3 potentiometer showed a maximum error of 0.2 mV in 200 mV. Routine calibration of the digital voltmeter was made using the slide wire of the Beckman pH meter, and this did not change more than 0.2 mV during the course of the day. The liquid ion-exchange electrode was transferred back and forth between the test solution and a reference solution (usually 0.1M KCl) and the potential recorded as a function of time. Equilibrium appeared to be reached within 5 min, except in the most dilute solutions. A stable potential was reached more quickly if the electrode was shaken down (like a clinical thermometer) before it was wiped to remove solution. Matched Ag/AgCl electrodes prepared by the thermal electrolytic process<sup>64</sup> were used in the two cells, and were equilibrated with the solution to be measured for several hours before the liquid ion-exchange electrode was placed in the solution.

Solutions were prepared by weight (except for concentrations below 0.1M which were obtained by dilution) from ACS reagent grade salts (Fisher Certified). Concentrations were verified by potentiometric titration with standard AgNO<sub>3</sub>. The NaCl used contained less than 0.005% potassium and the KCl contained less than 0.005% sodium. Bromide content of both salts was less than 0.01% and iodide content was less than 0.002%. The pH of the solutions was between 5.5 and 6, and thus no interference was expected from hydrogen or hydroxyl ion.<sup>61</sup> All measurements were conducted in a water bath thermostated at  $25.0 \pm 0.1$  °C.

## C. Results

Table XXIX gives the complete set of experimental measurements, together with calculations (see Table XXXIII for the computer programs used in these calculations) of the mean activity coefficient of KCl in the mixed NaCl-KCl electrolyte. The results of measurements in solutions containing only KCl are given in Table XXX. The potential differences quoted are the average of four successive measurements (errors are standard deviations), except for those marked with an asterisk, which were made with a fresh sample of the ion exchanger and are the average of two measurements. (For these the error is the range.) Mean activity coefficients



Table XXIX. Activity Coefficient of KCl in NaCl-KCl Electrolytes at 25 °C

RUN = ".1MKNA"      NAK = ".1M"  
 SLP = -.4139      ALP = -.01      IS = 0.0945

I	IONIC STRENGTH	X <sub>2</sub>	-F	LOG $\gamma_{21}$	LOG $\gamma_{21}$ (COR)
0	0.0936	1.0000	0.00	-0.1111	0.0000
1	0.0940	0.6798	11.80	-0.1290	-0.1292
2	0.0940	0.6798	13.10	-0.1400	-0.1402
3	0.0940	0.6798	13.00	-0.1391	-0.1393
4	0.0940	0.6798	13.70	-0.1451	-0.1453
5	0.0940	0.6798	14.00	-0.1476	-0.1478
6	0.0940	0.6798	13.00	-0.1391	-0.1393
7	0.0940	0.6798	12.50	-0.1349	-0.1351
8	0.0940	0.6798	14.00	-0.1476	-0.1478
9	0.0942	0.5061	17.10	-0.1108	-0.1109
10	0.0942	0.5061	17.00	-0.1099	-0.1100
11	0.0942	0.5061	18.00	-0.1184	-0.1185
12	0.0942	0.5061	17.90	-0.1175	-0.1176
13	0.0942	0.5061	18.00	-0.1184	-0.1185
14	0.0942	0.5061	17.70	-0.1159	-0.1160
15	0.0946	0.2572	33.10	-0.1005	-0.1005
16	0.0946	0.2572	33.30	-0.1022	-0.1022
17	0.0946	0.2572	33.90	-0.1073	-0.1072
18	0.0946	0.2572	33.80	-0.1064	-0.1064
19	0.0946	0.2572	33.60	-0.1047	-0.1047
20	0.0946	0.2572	33.70	-0.1056	-0.1056
21	0.0948	0.1188	51.10	-0.0857	-0.0856
22	0.0948	0.1188	51.70	-0.0908	-0.0907
23	0.0948	0.1188	51.70	-0.0908	-0.0907
24	0.0948	0.1188	52.20	-0.0950	-0.0949
25	0.0948	0.1188	51.20	-0.0866	-0.0865
26	0.0948	0.1188	51.50	-0.0891	-0.0890
27	0.0949	0.0434	75.60	-0.0745	-0.0743
28	0.0949	0.0434	76.10	-0.0787	-0.0785
29	0.0949	0.0434	76.10	-0.0787	-0.0785
30	0.0949	0.0434	76.20	-0.0795	-0.0794
31	0.0949	0.0434	76.00	-0.0778	-0.0777
32	0.0949	0.0434	75.90	-0.0770	-0.0769
33	0.0949	0.0128	104.70	-0.0553	-0.0551
34	0.0949	0.0128	103.80	-0.0477	-0.0475
35	0.0949	0.0128	106.30	-0.0688	-0.0686
36	0.0949	0.0128	106.80	-0.0730	-0.0729
37	0.0949	0.0128	106.10	-0.0671	-0.0669
38	0.0949	0.0012	153.70	0.0448	0.0450
39	0.0949	0.0012	154.10	0.0414	0.0416
40	0.0949	0.0012	138.70	0.1716	0.1718
41	0.0949	0.0012	139.00	0.1691	0.1693
42	0.0949	0.0012	135.90	0.1953	0.1955
43	0.0949	0.0012	136.70	0.1885	0.1887
44	0.0949	0.0012	135.60	0.1978	0.1980
45	0.0949	0.0012	134.50	0.2071	0.2073

Table XXIX (Cont.)

RUN = '.5MKNA'      NAK = '.5M'  
 SLP = -0.1053      ALP = -0.013      IS = 0.4756

I	IONIC STRENGTH	X <sub>2</sub>	-E	LOG $\gamma_{21}$	LOG $\gamma_{21}(\text{COR})$
0	0.4854	1.0000	0.00	-0.1864	0.0000
1	0.4809	0.7309	7.80	-0.1802	-0.1796
2	0.4809	0.7309	7.70	-0.1793	-0.1788
3	0.4809	0.7309	6.90	-0.1726	-0.1720
4	0.4809	0.7309	6.80	-0.1717	-0.1712
5	0.4809	0.7309	6.00	-0.1650	-0.1644
6	0.4771	0.4984	17.20	-0.1730	-0.1729
7	0.4771	0.4984	16.00	-0.1629	-0.1627
8	0.4771	0.4984	15.90	-0.1620	-0.1619
9	0.4735	0.2797	30.40	-0.1560	-0.1562
10	0.4735	0.2797	30.30	-0.1551	-0.1553
11	0.4735	0.2797	31.70	-0.1669	-0.1671
12	0.4735	0.2797	31.60	-0.1661	-0.1663
13	0.4713	0.1409	48.30	-0.1563	-0.1567
14	0.4713	0.1409	48.10	-0.1546	-0.1550
15	0.4713	0.1409	48.50	-0.1580	-0.1584
16	0.4713	0.1409	48.60	-0.1588	-0.1592
17	0.4702	0.0707	64.60	-0.1433	-0.1438
18	0.4702	0.0707	64.70	-0.1442	-0.1447
19	0.4702	0.0707	64.60	-0.1433	-0.1438
20	0.4702	0.0707	68.50	-0.1763	-0.1768
21	0.4702	0.0707	68.60	-0.1771	-0.1776
22	0.4693	0.0177	98.00	-0.1246	-0.1252
23	0.4693	0.0177	96.80	-0.1145	-0.1151
24	0.4693	0.0177	97.10	-0.1170	-0.1176
25	0.4693	0.0177	94.50	-0.0950	-0.0956

Notes:

RUN = name of source data file.

NAK = name of a scratch file prepared during the calculation.

SLP =  $\partial \log \gamma_{20} / \partial m_2$ .

ALP = approximate value for  $\alpha_{12}$ .

IS = ionic strength to which values in last column are corrected.

E = observed EMF difference between test and reference (point zero) solutions.

X<sub>2</sub> =  $m_2 / (m_1 + m_2)$  = ionic strength fraction of KCl.

Table XXIX (Cont.)

RUN = '1MKNA'      NAK = '1M'  
 SLP = -0.00500      ALP = -0.0095      IS = 1.0096

I	IONIC STRENGTH	X <sub>2</sub>	-F	LOG $\gamma_{21}$	LOG $\gamma_{21}$ (COR)
0	1.0241	1.0000	0.00	-0.2204	0.0000
1	1.0174	0.7056	7.90	-0.2086	-0.2082
2	1.0174	0.7056	8.00	-0.2095	-0.2091
3	1.0174	0.7056	7.70	-0.2069	-0.2066
4	1.0174	0.7056	7.40	-0.2044	-0.2040
5	1.0174	0.7056	7.30	-0.2035	-0.2032
6	1.0142	0.5608	13.40	-0.2038	-0.2036
7	1.0142	0.5608	13.20	-0.2021	-0.2019
8	1.0142	0.5608	13.30	-0.2030	-0.2028
9	1.0142	0.5608	13.50	-0.2047	-0.2045
10	1.0142	0.5608	13.00	-0.2004	-0.2002
11	1.0142	0.5608	13.10	-0.2013	-0.2011
12	1.0073	0.2514	31.60	-0.1805	-0.1806
13	1.0073	0.2514	30.80	-0.1737	-0.1738
14	1.0073	0.2514	31.50	-0.1797	-0.1797
15	1.0073	0.2514	31.40	-0.1788	-0.1789
16	1.0073	0.2514	30.90	-0.1746	-0.1747
17	1.0073	0.2514	31.10	-0.1763	-0.1764
18	1.0042	0.1094	50.70	-0.1600	-0.1602
19	1.0042	0.1094	50.90	-0.1616	-0.1619
20	1.0042	0.1094	49.30	-0.1481	-0.1483
21	1.0042	0.1094	49.40	-0.1490	-0.1492
22	1.0042	0.1094	50.80	-0.1608	-0.1610
23	1.0030	0.0582	63.50	-0.1304	-0.1307
24	1.0030	0.0582	63.70	-0.1321	-0.1324
25	1.0030	0.0582	65.20	-0.1448	-0.1451
26	1.0030	0.0582	66.50	-0.1558	-0.1561
27	1.0030	0.0582	66.40	-0.1549	-0.1552
28	1.0030	0.0582	67.00	-0.1600	-0.1603
29	1.0030	0.0582	67.10	-0.1609	-0.1611
30	1.0030	0.0582	65.10	-0.1440	-0.1442
31	1.0023	0.0225	86.40	-0.1179	-0.1182
32	1.0023	0.0225	85.80	-0.1128	-0.1131
33	1.0023	0.0225	87.20	-0.1246	-0.1249
34	1.0023	0.0225	87.50	-0.1272	-0.1275
35	1.0018	0.0010	148.00	0.0317	0.0314
36	1.0018	0.0010	148.20	0.0300	0.0297
37	1.0018	0.0010	146.80	0.0419	0.0415
38	1.0018	0.0010	146.70	0.0427	0.0424
39	1.0018	0.0010	147.40	0.0368	0.0365
40	1.0018	0.0010	147.20	0.0385	0.0382
41	1.0018	0.0005	160.20	0.0745	0.0742
42	1.0018	0.0005	160.30	0.0736	0.0733
43	1.0018	0.0005	160.10	0.0753	0.0750

Table XXIX (Cont.)

RUN = '2MKNA'      NAK = '2M'  
 SLP = -0.0176      ALP = -0.0084      IS = 1.5881

I	IONIC STRENGTH	X <sub>2</sub>	-E	LOG $\gamma_{21}$	LOG $\gamma_{21}$ (OR)
0	1.5687	1.0000	0.00	-0.2360	0.0000
1	1.5771	0.7265	6.10	-0.2205	-0.2206
2	1.5771	0.7265	5.60	-0.2162	-0.2164
3	1.5771	0.7265	5.80	-0.2179	-0.2181
4	1.5771	0.7265	5.70	-0.2171	-0.2172
5	1.5843	0.4927	14.00	-0.2049	-0.2050
6	1.5843	0.4927	14.10	-0.2058	-0.2058
7	1.5843	0.4927	14.20	-0.2066	-0.2067
8	1.5843	0.4927	14.30	-0.2074	-0.2075
9	1.5843	0.4927	13.20	-0.1981	-0.1982
10	1.5843	0.4927	13.10	-0.1973	-0.1974
11	1.5926	0.2271	30.20	-0.1759	-0.1759
12	1.5926	0.2271	29.50	-0.1700	-0.1700
13	1.5926	0.2271	29.70	-0.1717	-0.1717
14	1.5926	0.2271	29.20	-0.1675	-0.1674
15	1.5947	0.1622	34.40	-0.1389	-0.1388
16	1.5947	0.1622	35.00	-0.1440	-0.1439
17	1.5947	0.1622	35.60	-0.1491	-0.1490
18	1.5947	0.1622	36.00	-0.1524	-0.1524
19	1.5947	0.1622	36.80	-0.1582	-0.1581
20	1.5947	0.1622	36.90	-0.1600	-0.1600
21	1.5947	0.1622	35.70	-0.1489	-0.1488
22	1.5978	0.0625	58.70	-0.1381	-0.1380
23	1.5978	0.0625	58.30	-0.1348	-0.1347
24	1.5978	0.0625	56.50	-0.1195	-0.1194
25	1.5978	0.0625	56.40	-0.1187	-0.1186
26	1.5978	0.0625	57.00	-0.1238	-0.1237
27	1.5978	0.0625	57.10	-0.1246	-0.1245
28	1.5991	0.0218	77.00 ?	-0.0645 ?	-0.0644 ?
29	1.5991	0.0218	82.10	-0.1076	-0.1075
30	1.5991	0.0218	82.30	-0.1093	-0.1092
31	1.5991	0.0218	82.20	-0.1084	-0.1083
32	1.5991	0.0218	82.10	-0.1076	-0.1075

Table XXIX (Cont.)

RUN = '4MKNA'      NAK = '4M'  
 SLP = 0.0090      ALP = -0.0090      IS = 4.1605

I	IONIC STRENGTH	X <sub>2</sub>	-E	LOG $\gamma_{21}$	LOG $\gamma_{21}$ (COR)
0	4.2278	1.0000	0.00	-0.2375	0.0000
1	4.2027	0.7780	4.10	-0.2151	-0.2156
2	4.2027	0.7780	4.30	-0.2168	-0.2172
3	4.2027	0.7780	5.20	-0.2244	-0.2249
4	4.2027	0.7780	4.90	-0.2219	-0.2223
5	4.2027	0.7780	4.40	-0.2176	-0.2181
6	4.1756	0.5361	11.50	-0.1940	-0.1942
7	4.1756	0.5361	11.90	-0.1974	-0.1976
8	4.1756	0.5361	12.20	-0.1999	-0.2001
9	4.1756	0.5361	12.50	-0.2024	-0.2026
10	4.1756	0.5361	11.60	-0.1948	-0.1950
11	4.1756	0.5361	11.20	-0.1914	-0.1916
12	4.1756	0.5361	11.10	-0.1906	-0.1908
13	4.1482	0.2887	24.80	-0.1691	-0.1690
14	4.1482	0.2887	24.90	-0.1700	-0.1698
15	4.1482	0.2887	22.50	-0.1497	-0.1495
16	4.1482	0.2887	22.40	-0.1489	-0.1487
17	4.1482	0.2887	22.50	-0.1497	-0.1495
18	4.1482	0.2887	23.00	-0.1539	-0.1537
19	4.1299	0.1212	40.80	-0.1140	-0.1135
20	4.1299	0.1212	43.20	-0.1343	-0.1338
21	4.1299	0.1212	38.00	-0.0904	-0.0899
22	4.1299	0.1212	40.90	-0.1149	-0.1144
23	4.1299	0.1212	41.00	-0.1157	-0.1152
24	4.1229	0.0572	60.70	-0.1186	-0.1180
25	4.1229	0.0572	60.50	-0.1169	-0.1163
26	4.1229	0.0572	61.10	-0.1220	-0.1213
27	4.1229	0.0572	61.20	-0.1228	-0.1222
28	4.1182	0.0134	92.50	-0.0712	-0.0705
29	4.1182	0.0134	92.30	-0.0695	-0.0688
30	4.1182	0.0134	91.20	-0.0602	-0.0595
31	4.1182	0.0134	91.10	-0.0584	-0.0586
32	4.1182	0.0134	132.00 ?	-0.4051 ?	-0.4044 ?
33	4.1182	0.0134	91.40	-0.0619	-0.0612

for KCl ( $\gamma_{\pm}$ ) were interpolated from the tables of Robinson and Stokes<sup>12</sup> for concentration above 0.1m and calculated from the Debye-Hückel theory (with  $a = 4$ ) for lower concentrations. The calculated values of potential were obtained using the Nernst equation:

$$E = E^0 + \frac{2}{F} \frac{RT}{\ln} \ln(m\gamma_{\pm}) \quad (69)$$

where  $m$  is the molal concentration of KCl, and  $E^0$  is evaluated using the known concentration and activity coefficient of the reference solution.

Table XXX. Measurements in KCl Solutions at 25 °C

$m_{\text{KCl}}$	$\gamma_{\pm}$	$\Delta E_{\text{obs}}$ , mV	$\Delta E_{\text{calc}}$ , mV	Error, mV
4.228	0.579	$166.6 \pm 1.6$	180.8	-14.2
1.569	0.581	$119.6 \pm 3.0$	130.0	-10.4
1.569	0.581	$123.0 \pm 0.1^*$	130.0	-7.0
1.024	0.602	$98.2 \pm 0.6$	110.0	-11.8
0.4854	0.651	$68.0 \pm 0.7$	75.6	-7.6
0.4854	0.651	$70.1 \pm 0.1^*$	75.6	-5.5
0.0936	0.774	0	0	0
0.00936	0.899	$-95.5 \pm 0.9$	-110.6	+15.1
$9.36 \times 10^{-4}$	0.963	$-201.0 \pm 0.8$	-225.4	+15.3
$9.36 \times 10^{-5}$	0.989	$-330.6 \pm 2.3$	-342.4	+11.8
$9.36 \times 10^{-5}$	0.989	$-332.8 \pm 0.3^*$	-342.4	+9.6

\* Fresh exchanger.

Systematic deviations from the Nernst equation are clearly apparent in the data of Table XXX. These are in a direction opposite to the observed potential differences, and indicate that the liquid ion exchanger is somewhat permeable to chloride as well as to potassium ion. The deviations are smaller if the ion exchanger is fresh. At concentrations below  $10^{-5}$  m, deviations are in the direction of still more positive potentials<sup>59</sup> indicating that the ion exchanger contributes a finite amount of potassium ion to the test solution.

Empirically, a slope of approximately 90% of the Nernstian slope provides a relatively good fit ( $\pm 2$  mV) to the experimental data over the range from 0.001 to 4.3m. However, this slope depends on the age of the ion exchanger (e.g., 95% for fresh and 85% for aged material) and thus should be determined at the time of measurement if accurate analytical results are desired.

The measurements made in NaCl-KCl mixed electrolytes are summarized in Table XXXI. Each entry is the average of four to eight separate measurements. For each ionic strength, the reference solution was the KCl stock solution (first entry in each group). The mean activity coefficient ( $\gamma_{21}$ ) of KCl in the mixed electrolyte was calculated assuming that the Nernst

Table XXXI. Mean Activity of Coefficients of KCl in NaCl-KCl Electrolytes

Total Ionic Strength	$X_2$	$-E$ , mV	$-\log \gamma_{2,1}$	$-\log \gamma_{2,1}$ (corrected)	$K_s$
0.0936	1.0000	0	0.1111	0.1115	—
0.0940	0.6798	13.1	0.1403	0.1405	—
0.0942	0.5061	17.6	0.1152	0.1153	—
0.0946	0.2572	33.6	0.1045	0.1044	—
0.0948	0.1188	51.6	0.0897	0.0896	0.017
0.0949	0.0434	76.0	0.0777	0.0776	0.0085
0.0949	0.0128	105.5	0.0624	0.0622	0.0035
0.0949	0.0012	141.0	—	—	0.0029
0.4854	1.0000	0	0.1864	0.1854	—
0.4809	0.7309	7.0	0.1738	0.1732	—
0.4771	0.4984	16.4	0.1660	0.1658	—
0.4735	0.2797	31.0	0.1610	0.1612	—
0.4713	0.1409	48.4	0.1569	0.1573	0.0069
0.4702	0.0707	66.2	0.1568	0.1573	0.0032
0.4693	0.0177	96.6	0.1128	0.1133	0.0041
1.0241	1.0000	0	0.2204	0.2197	—
1.0174	0.7056	7.7	0.2066	0.2062	—
1.0142	0.5608	13.3	0.2026	0.2023	—
1.0073	0.2514	31.2	0.1772	0.1772	—
1.0042	0.1094	50.2	0.1559	0.1561	—
1.0030	0.0582	65.5	0.1479	0.1481	—
1.0023	0.0225	86.7	0.1206	0.1209	—
1.0018	0.0010	147.4	—	—	0.0018
1.0018	0.0005	160.2	—	—	0.0012
1.5687	1.0000	0	0.2360	0.2363	—
1.5771	0.7265	5.8	0.2180	0.2181	—
1.5843	0.4927	13.8	0.2034	0.2034	—
1.5926	0.2271	29.7	0.1713	0.1713	—
1.5947	0.1622	35.8	0.1505	0.1504	0.075
1.5978	0.0625	57.3	0.1266	0.1264	0.034
1.5991	0.0218	82.2	0.1082	0.1081	0.014
4.2279	1.0000	0	0.2375	0.2382	—
4.2027	0.7780	4.6	0.2192	0.2196	—
4.1756	0.5361	11.7	0.1957	0.1960	—
4.1482	0.2887	23.3	0.1569	0.1567	—
4.1299	0.1212	40.8	0.1139	0.1133	0.039
4.1229	0.0572	60.9	0.1201	0.1195	0.015
4.1182	0.0134	91.7	0.0644	0.0637	0.0065

Note: Component 1 is NaCl, component 2 is KCl.  $X_2 = m_2/(m_1 + m_2)$ .  $\gamma_{2,1}$  values are corrected to ionic strengths of 0.0945, 0.4756, 1.0096, 1.5881, or 4.1605 (depending on the group) using isopiestic data to determine the correction factors.<sup>65</sup>  $K_s$  is calculated as described in text.  $E$  is potential in test solution minus potential in reference solution (first entry in each group).

equation was obeyed with the theoretical slope and that the potassium-selective liquid ion exchanger did not respond at all to sodium ion.<sup>34</sup> The mean activity coefficient ( $\gamma_{20}$ ) of KCl in the reference solution was obtained as described above. The deviations of the observed EMF values from the theoretical values (Table XXXII) are plotted in Fig. 15. These were calculated assuming that the isopiestic data<sup>7, 65</sup> for the mean activity coefficients of KCl ( $\gamma_{21}$ ) and NaCl ( $\gamma_{12}$ ) in mixed electrolytes were corrected. Individual measurements have been plotted to show the consistency of results in a given solution. At higher Na/K ratios, the deviations are always in the same direction (the observed potential is more positive than the calculated potential), consistent with the hypothesis of partial transport of  $\text{Na}^+$  along with  $\text{K}^+$ .

The selectivity ratio of this ion-exchange electrode has been reported<sup>59</sup> to be  $2 \times 10^{-4}$  (for Na versus K). This value is obtained by comparing the potential of the electrode in a solution containing only KCl with that in a solution containing KCl at the same concentration together with 0.1M NaCl. A line calculated using this value is plotted in Fig. 15. Our data can also be used to calculate a selectivity ratio, but at the high ionic strengths we are considering, we must take account of the differences in activity coefficient between NaCl and KCl in the same electrolyte mixture. We have defined the selectivity ratio ( $K_s$ ) by the equation<sup>34</sup>

$$E = E^0 + \frac{RT}{F} \ln \{ (m_2 \gamma_{21}^2 + K_s m_1 \gamma_{12}^2) (m_1 + m_2) \} \quad (70)$$

where  $m_1$  is the molal concentration of NaCl,  $m_2$  is the molal concentration of KCl, and the other symbols are as defined above. The values obtained for  $K_s$  are listed in Table XXXI for solutions where the Na/K ratio is greater than 5. For solutions consisting mostly of KCl, the uncertainties in the mean activity coefficient are much greater than the effects of selectivity.

Note that the selectivity ratio is relatively independent of total ionic strength, but depends in a consistent way on the Na/K ratio. Extrapolation of  $K_s$  to zero KCl concentration is shown in Fig. 16. Values between  $5 \times 10^{-4}$  and  $4 \times 10^{-3}$  are consistent with the data. Although this is slightly higher than the published value,<sup>61</sup> a slightly lower extrapolated value might be obtained if fresh exchanger were used for each measurement and correction were made for residual  $\text{K}^+$  in the NaCl.

Since the total ionic strength is held constant for each set of measurements, the gradient of chloride concentration across the ion-exchange membrane is also constant, and thus deviations from Nernstian behavior due to chloride transport should contribute negligibly to these measurements. The fact that systematic deviations from the calculated potentials are observed (or alternatively, that the selectivity ratio is composition dependent) indicates that the transport mechanism is more complicated than might be supposed on the basis of a simple ion exchange model.



Table XXXII. Deviation of Experimental Data From Isopiestic Values

KSL = 0								
IS	XKCL	L20	L21	L12	DE	DEC	DDE	A21
0.0949	1.0000	-.1096	-.1096	-.1081	0.0	0.0	0.0	0.00000
0.0940	0.6798	-.1096	-.1088	-.1069	11.8	10.3	-1.5	-.02808
0.0940	0.6798	-.1096	-.1088	-.1069	13.1	10.3	-2.8	-.02808
0.0940	0.6798	-.1096	-.1088	-.1069	13.0	10.3	-2.7	-.02808
0.0940	0.6798	-.1096	-.1088	-.1069	13.7	10.3	-3.4	-.02808
0.0940	0.6798	-.1096	-.1088	-.1069	14.0	10.3	-3.7	-.02808
0.0940	0.6798	-.1096	-.1088	-.1069	13.0	10.3	-2.7	-.02808
0.0940	0.6798	-.1096	-.1088	-.1069	12.5	10.3	-2.2	-.02808
0.0940	0.6798	-.1096	-.1088	-.1069	14.0	10.3	-3.7	-.02808
0.0942	0.5061	-.1096	-.1086	-.1066	17.1	17.8	0.7	-.02195
0.0942	0.5061	-.1096	-.1086	-.1066	17.0	17.8	0.8	-.02195
0.0942	0.5061	-.1096	-.1086	-.1066	18.0	17.8	-0.2	-.02195
0.0942	0.5061	-.1096	-.1086	-.1066	17.9	17.8	-0.1	-.02195
0.0942	0.5061	-.1096	-.1086	-.1066	18.0	17.8	-0.2	-.02195
0.0942	0.5061	-.1096	-.1086	-.1066	17.7	17.8	0.1	-.02195
0.0946	0.2572	-.1096	-.1084	-.1061	33.1	34.9	1.8	-.01751
0.0946	0.2572	-.1096	-.1084	-.1061	33.3	34.9	1.6	-.01751
0.0946	0.2572	-.1096	-.1084	-.1061	33.9	34.9	1.0	-.01751
0.0946	0.2572	-.1096	-.1084	-.1061	33.8	34.9	1.1	-.01751
0.0946	0.2572	-.1096	-.1084	-.1061	33.6	34.9	1.3	-.01751
0.0946	0.2572	-.1096	-.1084	-.1061	33.7	34.9	1.2	-.01751
0.0948	0.1188	-.1096	-.1083	-.1058	51.1	54.6	3.5	-.01625
0.0948	0.1188	-.1096	-.1083	-.1058	51.7	54.6	2.9	-.01625
0.0948	0.1188	-.1096	-.1083	-.1058	51.7	54.6	2.9	-.01625
0.0948	0.1188	-.1096	-.1083	-.1058	52.2	54.6	2.4	-.01625
0.0948	0.1188	-.1096	-.1083	-.1058	51.2	54.6	3.4	-.01625
0.0948	0.1188	-.1096	-.1083	-.1058	51.5	54.6	3.1	-.01625
0.0949	0.0434	-.1096	-.1082	-.1057	75.6	80.4	4.8	-.01576
0.0949	0.0434	-.1096	-.1082	-.1057	76.1	80.4	4.3	-.01576
0.0949	0.0434	-.1096	-.1082	-.1057	76.1	80.4	4.3	-.01576
0.0949	0.0434	-.1096	-.1082	-.1057	76.2	80.4	4.2	-.01576
0.0949	0.0434	-.1096	-.1082	-.1057	76.0	80.4	4.4	-.01576
0.0949	0.0434	-.1096	-.1082	-.1057	75.9	80.4	4.5	-.01576
0.0949	0.0128	-.1096	-.1081	-.1056	104.7	111.8	7.1	-.01576
0.0949	0.0128	-.1096	-.1081	-.1056	103.8	111.8	8.0	-.01576
0.0949	0.0128	-.1096	-.1081	-.1056	106.3	111.8	5.5	-.01576
0.0949	0.0128	-.1096	-.1081	-.1056	106.8	111.8	5.0	-.01576
0.0949	0.0128	-.1096	-.1081	-.1056	106.1	111.8	5.7	-.01576
0.0949	0.0012	-.1096	-.1081	-.1056	153.7	172.6	18.9	-.01576
0.0949	0.0012	-.1096	-.1081	-.1056	154.1	172.6	18.5	-.01576
0.0949	0.0012	-.1096	-.1081	-.1056	138.7	172.6	33.9	-.01576
0.0949	0.0012	-.1096	-.1081	-.1056	139.0	172.6	33.6	-.01576
0.0949	0.0012	-.1096	-.1081	-.1056	135.9	172.6	36.7	-.01576
0.0949	0.0012	-.1096	-.1081	-.1056	136.7	172.6	35.9	-.01576
0.0949	0.0012	-.1096	-.1081	-.1056	135.6	172.6	37.0	-.01576

Table XXXII (Cont.)

KSL = 0								
IS	XKCL	L20	L21	L12	DE	DEC	DDE	A21
0.4691	1.0000	-.1814	-.1814	-.1744	0.0	0.0	0.0	0.0000
0.4809	0.7309	-.1814	-.1809	-.1723	7.8	6.7	-1.1	-.00397
0.4809	0.7309	-.1814	-.1809	-.1723	7.7	6.7	-1.0	-.00397
0.4809	1.7309	-.1814	-.1809	-.1723	6.9	6.7	-0.2	-.00397
0.4809	0.7309	-.1814	-.1809	-.1723	6.8	6.7	-0.1	-.00397
0.4809	0.7309	-.1814	-.1809	-.1723	6.0	6.7	0.7	-.00397
0.4771	0.4984	-.1814	-.1790	-.1693	17.2	16.7	-0.5	-.00996
0.4771	0.4984	-.1814	-.1790	-.1693	16.0	16.7	0.7	-.00996
0.4771	0.4984	-.1814	-.1790	-.1693	15.9	16.7	0.8	-.00996
0.4735	0.2797	-.1814	-.1773	-.1664	30.4	31.8	1.4	-.01212
0.4735	0.2797	-.1814	-.1773	-.1664	30.3	31.8	1.5	-.01212
0.4735	0.2797	-.1814	-.1773	-.1664	31.7	31.8	0.1	-.01212
0.4735	0.2797	-.1814	-.1773	-.1664	31.6	31.8	0.2	-.01212
0.4713	0.1409	-.1814	-.1762	-.1646	48.3	49.5	1.2	-.01293
0.4713	0.1409	-.1814	-.1762	-.1646	48.1	49.5	1.4	-.01293
0.4713	0.1409	-.1814	-.1762	-.1646	48.5	49.5	1.0	-.01293
0.4713	0.1409	-.1814	-.1762	-.1646	48.6	49.5	0.9	-.01293
0.4702	0.0707	-.1814	-.1756	-.1637	64.6	67.3	2.7	-.01325
0.4702	0.0707	-.1814	-.1756	-.1637	64.7	67.3	2.6	-.01325
0.4702	0.0707	-.1814	-.1756	-.1637	64.6	67.3	2.7	-.01325
0.4702	0.0707	-.1814	-.1756	-.1637	68.5	67.3	-1.2	-.01325
0.4702	0.0707	-.1814	-.1756	-.1637	68.6	67.3	-1.3	-.01325
0.4693	0.0177	-.1814	-.1752	-.1630	98.0	102.9	4.9	-.01348
0.4693	0.0177	-.1814	-.1752	-.1630	96.8	102.9	6.1	-.01348
0.4693	0.0177	-.1814	-.1752	-.1630	97.1	102.9	5.8	-.01348

Notes:

IS = total ionic strength

XKCL =  $X_2$ L20 =  $\log \gamma_{20}$ L21 =  $\log \gamma_{21}$ L12 =  $\log \gamma_{12}$ Calculated using equations of Rush (ORNL-4402)  
based on isopiestic data of Robinson.DE =  $-E_{\text{obs}}$  (see Table XXX)DEC =  $-E_{\text{calc}}$ DDE = difference:  $E_{\text{obs}} - E_{\text{calc}}$ A21 =  $\alpha_{21}$  calculated from equations of Rush.

Table XXXII (Cont.)

KSL = 0								
IS	XKCL	L20	L21	L12	DE	DEC	DDE	A21
1.0018	1.0000	-.2172	-.2172	-.2038	0.0	0.0	0.0	0.00000
1.0174	0.7056	-.2172	-.2146	-.1976	7.9	7.9	0.0	-.00874
1.0174	0.7056	-.2172	-.2146	-.1976	8.0	7.9	-0.1	-.00874
1.0174	0.7056	-.2172	-.2146	-.1976	7.7	7.9	0.2	-.00874
1.0174	0.7056	-.2172	-.2146	-.1976	7.4	7.9	0.5	-.00874
1.0174	0.7056	-.2172	-.2146	-.1976	7.3	7.9	0.6	-.00874
1.0142	0.5608	-.2172	-.2128	-.1941	13.4	13.7	0.3	-.00983
1.0142	0.5608	-.2172	-.2128	-.1941	13.2	13.7	0.5	-.00983
1.0142	0.5608	-.2172	-.2128	-.1941	13.3	13.7	0.4	-.00983
1.0142	0.5608	-.2172	-.2128	-.1941	13.5	13.7	0.2	-.00983
1.0142	0.5608	-.2172	-.2128	-.1941	13.0	13.7	0.7	-.00983
1.0142	0.5608	-.2172	-.2128	-.1941	13.1	13.7	0.6	-.00983
1.0073	0.2514	-.2172	-.2091	-.1868	31.6	34.2	2.6	-.01083
1.0073	0.2514	-.2172	-.2091	-.1868	30.8	34.2	3.4	-.01083
1.0073	0.2514	-.2172	-.2091	-.1868	31.5	34.2	2.7	-.01083
1.0073	0.2514	-.2172	-.2091	-.1868	31.4	34.2	2.8	-.01083
1.0073	0.2514	-.2172	-.2091	-.1868	30.9	34.2	3.3	-.01083
1.0073	0.2514	-.2172	-.2091	-.1868	31.1	34.2	3.1	-.01083
1.0042	0.1094	-.2172	-.2073	-.1835	50.7	55.5	4.8	-.01108
1.0042	0.1094	-.2172	-.2073	-.1835	50.9	55.5	4.6	-.01108
1.0042	0.1094	-.2172	-.2073	-.1835	49.3	55.5	6.2	-.01108
1.0042	0.1094	-.2172	-.2073	-.1835	49.4	55.5	6.1	-.01108
1.0042	0.1094	-.2172	-.2073	-.1835	50.8	55.5	4.7	-.01108
1.0030	0.0582	-.2172	-.2067	-.1823	63.5	71.7	8.2	-.01116
1.0030	0.0582	-.2172	-.2067	-.1823	63.7	71.7	8.0	-.01116
1.0030	0.0582	-.2172	-.2067	-.1823	65.2	71.7	6.5	-.01116
1.0030	0.0582	-.2172	-.2067	-.1823	66.5	71.7	5.2	-.01116
1.0030	0.0582	-.2172	-.2067	-.1823	66.4	71.7	5.3	-.01116
1.0030	0.0582	-.2172	-.2067	-.1823	67.0	71.7	4.7	-.01116
1.0030	0.0582	-.2172	-.2067	-.1823	67.1	71.7	4.6	-.01116
1.0030	0.0582	-.2172	-.2067	-.1823	65.1	71.7	6.6	-.01116
1.0023	0.0225	-.2172	-.2062	-.1815	86.4	96.1	9.7	-.01121
1.0023	0.0225	-.2172	-.2062	-.1815	85.8	96.1	10.3	-.01121
1.0023	0.0225	-.2172	-.2062	-.1815	87.2	96.1	8.9	-.01121
1.0023	0.0225	-.2172	-.2062	-.1815	87.5	96.1	8.6	-.01121
1.0018	0.0010	-.2172	-.2060	-.1809	148.0	176.1	28.1	-.01124
1.0018	0.0010	-.2172	-.2060	-.1809	148.2	176.1	27.9	-.01124
1.0018	0.0010	-.2172	-.2060	-.1809	146.8	176.1	29.3	-.01124
1.0018	0.0010	-.2172	-.2060	-.1809	146.7	176.1	29.4	-.01124
1.0018	0.0010	-.2172	-.2060	-.1809	147.4	176.1	28.7	-.01124
1.0018	0.0010	-.2172	-.2060	-.1809	147.2	176.1	28.9	-.01124
1.0018	0.0005	-.2172	-.2060	-.1809	160.2	193.9	33.7	-.01124
1.0018	0.0005	-.2172	-.2060	-.1809	160.3	193.9	33.6	-.01124

Table XXXII (Cont.)

KSL = 0								
IS	XKCL	L20	L21	L12	DE	DEC	DDE	A21
1.5998	1.00000	-.2345	-.2345	-.2151	0.0	0.0	0.0	0.00000
1.5771	0.7265	-.2345	-.2300	-.2057	6.1	8.4	2.3	-.01035
1.5771	0.7265	-.2345	-.2300	-.2057	5.6	8.4	2.8	-.01035
1.5771	0.7265	-.2345	-.2300	-.2057	5.8	8.4	2.6	-.01035
1.5771	0.7265	-.2345	-.2300	-.2057	5.7	8.4	2.7	-.01035
1.5843	0.4927	-.2345	-.2266	-.1977	14.0	17.7	3.7	-.00984
1.5843	0.4927	-.2345	-.2266	-.1977	14.1	17.7	3.6	-.00984
1.5843	0.4927	-.2345	-.2266	-.1977	14.2	17.7	3.5	-.00984
1.5843	0.4927	-.2345	-.2266	-.1977	14.3	17.7	3.4	-.00984
1.5843	0.4927	-.2345	-.2266	-.1977	13.2	17.7	4.5	-.00984
1.5843	0.4927	-.2345	-.2266	-.1977	13.1	17.7	4.6	-.00984
1.5926	0.2271	-.2345	-.2225	-.1885	30.2	36.9	6.7	-.00971
1.5926	0.2271	-.2345	-.2225	-.1885	29.5	36.9	7.4	-.00971
1.5926	0.2271	-.2345	-.2225	-.1885	29.7	36.9	7.2	-.00971
1.5926	0.2271	-.2345	-.2225	-.1885	29.2	36.9	7.7	-.00971
1.5947	0.1622	-.2345	-.2215	-.1862	34.4	45.4	11.0	-.00971
1.5947	0.1622	-.2345	-.2215	-.1862	35.0	45.4	10.4	-.00971
1.5947	0.1622	-.2345	-.2215	-.1862	35.6	45.4	9.8	-.00971
1.5947	0.1622	-.2345	-.2215	-.1862	36.0	45.4	9.4	-.00971
1.5947	0.1622	-.2345	-.2215	-.1862	36.8	45.4	8.6	-.00971
1.5947	0.1622	-.2345	-.2215	-.1862	36.9	45.4	8.5	-.00971
1.5947	0.1622	-.2345	-.2215	-.1862	35.7	45.4	9.7	-.00971
1.5978	0.0625	-.2345	-.2199	-.1826	58.7	69.6	10.9	-.00971
1.5978	0.0625	-.2345	-.2199	-.1826	58.3	69.6	11.3	-.00971
1.5978	0.0625	-.2345	-.2199	-.1826	56.5	69.6	13.1	-.00971
1.5978	0.0625	-.2345	-.2199	-.1826	56.4	69.6	13.2	-.00971
1.5978	0.0625	-.2345	-.2199	-.1826	57.0	69.6	12.6	-.00971
1.5978	0.0625	-.2345	-.2199	-.1826	57.1	69.6	12.5	-.00971
1.5991	0.0218	-.2345	-.2193	-.1811	77.0	96.5	19.5	-.00971
1.5991	0.0218	-.2345	-.2193	-.1811	82.1	96.5	14.4	-.00971
1.5991	0.0218	-.2345	-.2193	-.1811	82.3	96.5	14.2	-.00971
1.5991	0.0218	-.2345	-.2193	-.1811	82.2	96.5	14.3	-.00971

Table XXXII (Cont.)

KSL = 0								
IS	XKCL	L20	L21	L12	DE	DEC	DDE	A21
4.1167	1.0000	-.2357	-.2357	-.1955	0.0	0.0	0.0	0.00000
4.2027	0.7780	-.2357	-.2268	-.1730	4.1	4.3	0.2	-.00956
4.2027	0.7780	-.2357	-.2268	-.1730	4.3	4.3	0.0	-.00956
4.2027	0.7780	-.2357	-.2268	-.1730	5.2	4.3	-0.9	-.00956
4.2027	0.7780	-.2357	-.2268	-.1730	4.9	4.3	-0.6	-.00956
4.2027	0.7780	-.2357	-.2268	-.1730	4.4	4.3	-0.1	-.00956
4.1756	0.5361	-.2357	-.2177	-.1504	11.5	13.2	1.7	-.00930
4.1756	0.5361	-.2357	-.2177	-.1504	11.9	13.2	1.3	-.00930
4.1756	0.5361	-.2357	-.2177	-.1504	12.2	13.2	0.0	-.00930
4.1756	0.5361	-.2357	-.2177	-.1504	12.5	13.2	0.7	-.00930
4.1756	0.5361	-.2357	-.2177	-.1504	11.6	13.2	1.6	-.00930
4.1756	0.5361	-.2357	-.2177	-.1504	11.2	13.2	2.0	-.00930
4.1756	0.5361	-.2357	-.2177	-.1504	11.1	13.2	2.1	-.00930
4.1482	0.2887	-.2357	-.2079	-.1270	24.8	28.2	3.4	-.00943
4.1482	0.2887	-.2357	-.2079	-.1270	24.9	28.2	3.3	-.00943
4.1482	0.2887	-.2357	-.2079	-.1270	22.5	28.2	5.7	-.00943
4.1482	0.2887	-.2357	-.2079	-.1270	22.4	28.2	5.8	-.00943
4.1482	0.2887	-.2357	-.2079	-.1270	22.5	28.2	5.7	-.00943
4.1482	0.2887	-.2357	-.2079	-.1270	23.0	28.2	5.2	-.00943
4.1299	0.1212	-.2357	-.2009	-.1110	40.8	49.9	9.1	-.00959
4.1299	0.1212	-.2357	-.2009	-.1110	43.2	49.9	6.7	-.00959
4.1299	0.1212	-.2357	-.2009	-.1110	38.0	49.9	11.9	-.00959
4.1299	0.1212	-.2357	-.2009	-.1110	40.9	49.9	9.0	-.00959
4.1299	0.1212	-.2357	-.2009	-.1110	41.0	49.9	8.9	-.00959
4.1229	0.0572	-.2357	-.1982	-.1048	60.7	69.0	8.3	-.00965
4.1229	0.0572	-.2357	-.1982	-.1048	60.5	69.0	8.5	-.00965
4.1229	0.0572	-.2357	-.1982	-.1048	61.1	69.0	7.9	-.00965
4.1229	0.0572	-.2357	-.1982	-.1048	61.2	69.0	7.8	-.00965
4.1182	0.0134	-.2357	-.1963	-.1006	92.5	106.1	13.6	-.00969
4.1182	0.0134	-.2357	-.1963	-.1006	92.3	106.1	13.8	-.00969
4.1182	0.0134	-.2357	-.1963	-.1006	91.2	106.1	14.9	-.00969
4.1182	0.0134	-.2357	-.1963	-.1006	91.1	106.1	15.0	-.00969
4.1182	0.0134	-.2357	-.1963	-.1006	132.0	106.1	-25.9	-.00969

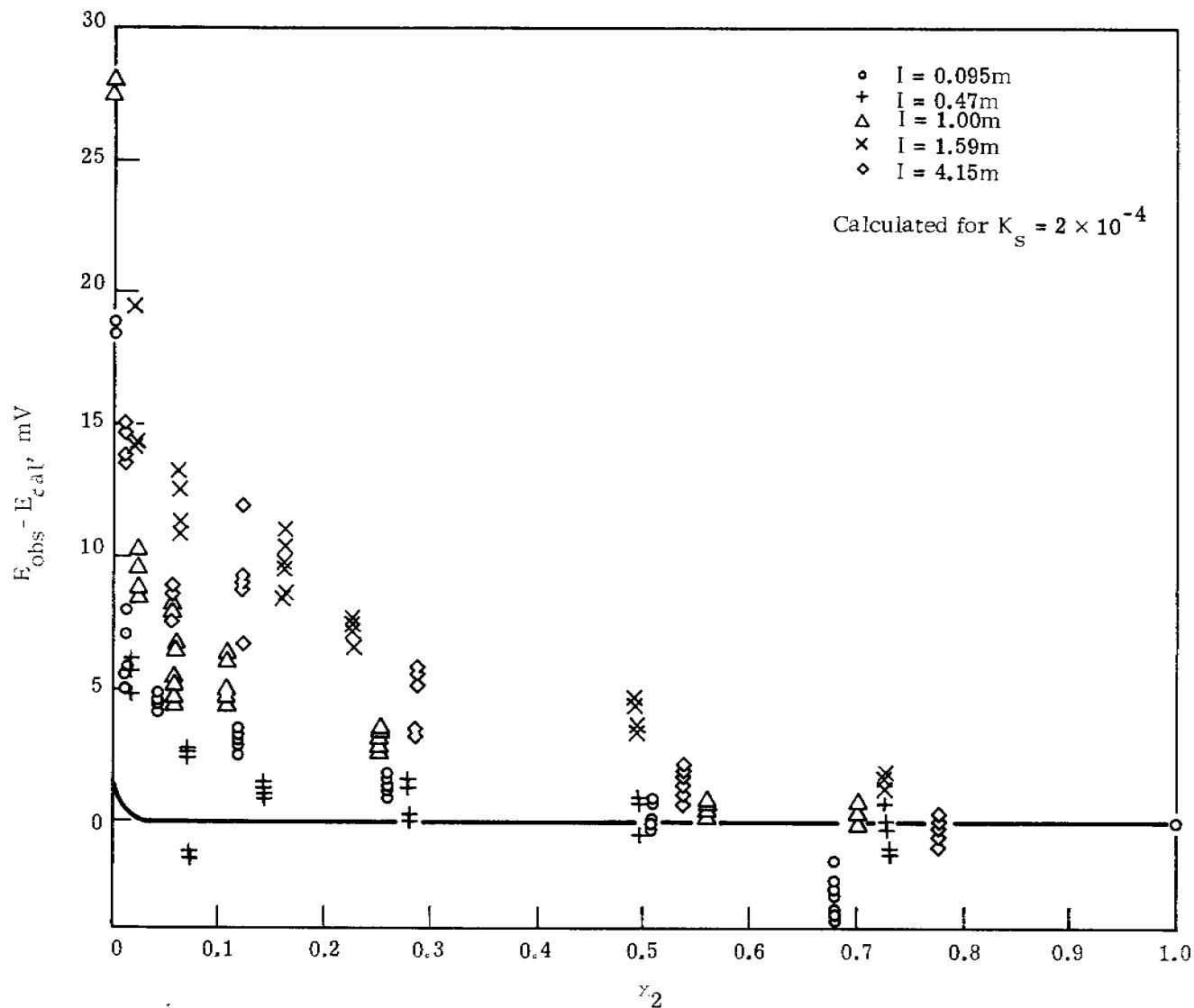


Fig. 15. Deviations of experimental measurements from calculated potential values based on the Nernst equation and isopiestic<sup>65</sup> data

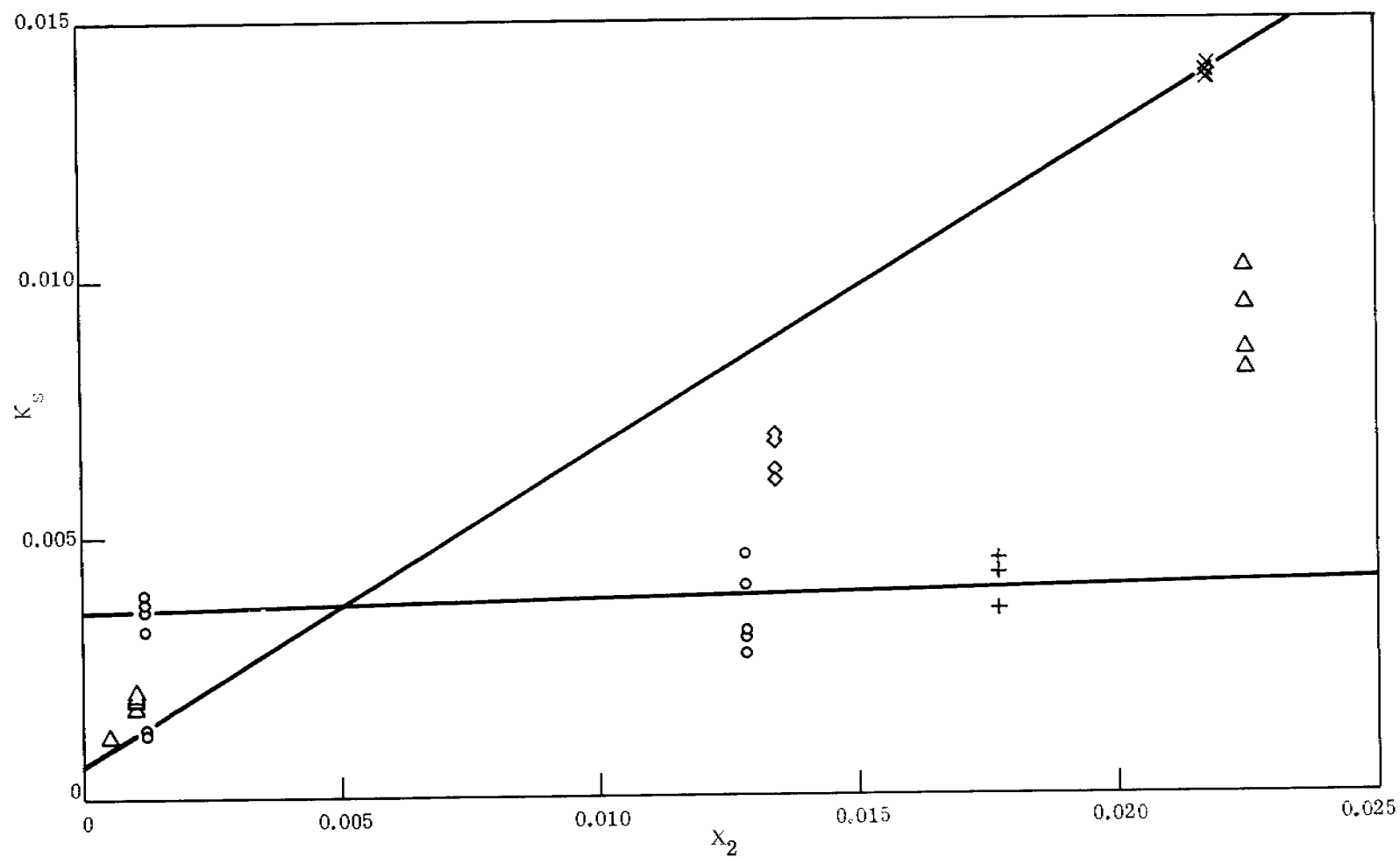


Fig. 16. Extrapolation of selectivity ratio to zero potassium content

Table XXXIII. Computer Program Used for Calculating the Mean Activity Coefficient of KCl in the Mixed NaCl-KCl Electrolyte

PROGRAM /K-NA/ 10/13/69 PAGE 1

>LOAD  
FROM /K-NA/  
>TYPE ALL

```

1.06 DO PART 19
1.1 OPEN NAK FOR INPUT AS FILE 1
1.15 READ FROM 1:N
1.22 DO PART 10
1.23 SDE = 0
1.235 PAGE
1.24 DEMAND KSL
1.25 TYPE IN FORM 1:
1.3 DO PART 2 FOR I = 1 TO N
1.4 CLOSE 1
1.5 SD = SQRT(SDE/(N*(N-1)))
1.51 TYPE SDE, SD
1.60 DO PART 5
1.605 PAGE
1.61 DONE

2.1 READ FROM 1: IS, FK, DE
2.2 DO PART 3 IF DE = 0
2.25 Y(1) = 1-FK
2.26 DO PART 11
2.31 DEA = 118.3*LOG10(IS0*G20)
2.32 DEB = 59.15*LOG10(FK *G21^2+KSL*(1-FK)*G12^2)
2.33 DEC = DEA - DEB -118.3*LOG10(IS)
2.34 Y(1) = 999 IF DE = 0
2.35 L20 = LOG10(G20), L12 = LOG10(G12), L21 = LOG10(G21),
A21 = (L20-L21)/(Y(1)*IS)
2.4 DDE = DEC-DE
2.41 SDE = SDE+ DDE^2
2.5 TYPE IN FORM 2: IS, FK, L20, L21, L12, DE, DEC, DDE, A21

3.1 IS0 = IS
3.21 Y (1) = 0
3.22 DO PART 11
3.3 G20 = G21

4.01 READ FROM 1: IS, FK, DE
4.02 DO PART 3 IF DE =0
4.03 Y(1) = 1-FK
4.04 DO PART 11
4.11 QA = (IS0*G20/IS)^2
4.12 QB = 10^-(DE/59.15)
4.13 QC = FK*G21^2
4.14 QD = (1-FK)*G12^2
4.15 L21 = LOG10(G21)
4.21 KSL=0 IF FK = 1
4.22 TO STEP 4.3 IF FK = 1
4.23 KSL = (QA*QB-QC)/QD
4.3 TYPE IN FORM 5: IS, FK, DE, L21, KSL

5.0 PAGE
5.01 DO PART 10
5.1 TYPE

```



Table XXXIII (Cont.)

PROGRAM /K-NA/ 10/13/69 PAGE 2

IS XKCL DE L21 KSL"

5.2 OPEN NAK FOR INPUT AS FILE 1

5.25 READ FROM 1: N

5.3 DO PART 4 FOR I = 1 TO N

5.4 CLOSE 1

10.01 S = -1.17082, AP = 1.5, A = 1, B = 2

10.02 LB1 = -0.0253, LB2 = -0.00299

10.03 A(1,1) = .03684, A(1,2) = -.06408

10.04 A(2,1) = .02108, A(2,2) = .05244

10.05 A(3,1) = -0.001304, A(3,2) = -0.01124

10.06 A(4,1) = 0, A(4,2) = 0.000918

11.01 BET = (LB1 + LB2\*IS)\*IS

11.02 BB = (LB1 + LB2\*IS/2)\*IS

11.03 SQI = AP\*SQRT(IS)

11.11 DO PART 12 FOR J = 1,2

11.22 Y(2) = 1 - Y(1)

11.31 J = A, K = B

11.32 DO PART 13

11.33 J = B, K = A

11.34 DO PART 13

11.41 G12 = EXP(LG(A)), G21 = EXP(LG(B))

12.01 AAA = 2\*S\*SQRT(IS)/(1+SQI) + 2\*A(1,J)\*IS + 1.5\*A(2,J)\*IS\*IS

12.02 AAB = 4\*A(3,J)\*IS^3/3 + 1.25\*A(4,J)\*IS^4

12.03 AA(J) = AAA + AAB

12.11 ALA = 2\*S/(AP^3\*IS)

12.12 ALB = 1 + SQI - 1/(1+SQI) - 2\*LOG(1+SQI)

12.13 ALC = A(1,J)\*IS + A(2,J)\*IS^2 + A(3,J)\*IS^3 + A(4,J)\*IS^4

12.14 AL(J) = ALA\*ALB + ALC

13.1 LG(J) = .5\*(AA(J)+(AL(K)-AL(J))\*Y(K)+BET\*Y(K)+(BB-BET)\*Y(K)^2)

19.04 DEMAND RUN

19.05 OPEN RUN FOR INPUT AS FILE 1

19.1 READ FROM 1: N, G, KR, NR

19.15 QQN = 1000/(1000 + (NR\*58.4428)), QQK = 1000/(1000 + (KR\*74.555)), QNA = (QQN\*NR), QK = (QQK\*KR)

19.2 READ FROM 1: X(I), Y(I) FOR I=1 TO N

19.3 READ FROM 1: E(I) FOR I=1 TO N

19.35 CLOSE 1

19.36 DEMAND NAK

19.37 OPEN NAK FOR OUTPUT AS FILE 2

19.38 WRITE ON 2: N

19.39 WRITE ON 2 IN FORM 30: NR, 1, 0

19.391 DEMAND SLP, ALP, IS

19.4 TYPE

I IONIC STRENGTH XKCL E LOG G12 LOG G12 COR"

19.45 TYPE IN FORM 3: 0, KR, 1, 0, LOG10(G), 0

19.51 DO PART 20 FOR I = 1 TO N

19.6 CLOSE 2

19.65 PAGE

20.10 WW = (X(I)\*QQK)+(Y(I)\*QQN), MNA = (QNA\*Y(I))/WW,  
MK = (QK\*X(I))/WW, FK = MK/(MNA+MK), FNA = MNA/(MNA+MK),

PROGRAM /K-NA/ 10/13/69 PAGE 3

```

      LGO = LOG10(KR*G) - .5*LOG10(MK*(MK+MNA)) - E(I)/118.3,
      IO = MNA+MK, LGC = LGO + ((SLP - (ALP*FNA))*(IS-10))
20.20 WRITE ON 2 IN FORM 30: IO, FK, E(I)
20.3 TYPE IN FORM 3: I, IO, FK, E(I), LGO, LGC

```

```

FORM 1:
  IS      XKCL      L20      L21      L12      DE      DEC      DDE      A21
FORM 2:
  ZZ.ZZZZ  ZZ.ZZZZ  Z.ZZZZ  Z.ZZZZ  Z.ZZZZ  ZZ.Z  ZZ.Z  ZZ.Z  Z.ZZZZ
FORM 3:
  ZZ      ZZ.ZZZZ      ZZ.ZZZZ      ZZ.ZZ      ZZ.ZZZZ      ZZ.ZZZZ
FORM 5:
  ZZ.ZZZZ  Z.ZZZZ  ZZ.Z  ZZ.ZZZZ  Z.ZZZZ
FORM 30:
  ZZ.ZZZZ      ZZ.ZZZZ      ZZ.ZZZZ

```

Note: This program incorporates modified versions of programs/R3/and /NACLKCL/, which were given in the Second Interim Report.

RUN = input file name, e. g., 'NACL.'

N = number of points.

G =  $\gamma_{20}$  in reference solution (KCl).

KR =  $m_2$  in KCl stock.

NR =  $m_1$  in NaCl stock.

X(I) = weight of NaCl stock.

Y(I) = weight of KCl stock.

E(I) = measured potential difference (reference-test);  $-E_{\text{obs}}$ .

SLP =  $\partial \log \gamma_{20} / \partial m_2$ .

ALP = approximate value of  $\alpha_{21}$ .

IS = ionic strength to which  $\gamma_{21}$  is to be corrected.

NAK = name of scratch file, e. g., 'SCRATCH.'

KSL = assumed selectivity ratio for calculating deviations of E.

SDE =  $\sum (E_{\text{obs}} - E_{\text{calc}})^2$ .

SD =  $\sqrt{\text{SDE} / (N(N-1))}$ .

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## VIII. PUBLICATIONS

The following publications have resulted from work done under this contract:

1. Activity Coefficient Measurements in Aqueous Sodium Chloride-Sodium Sulfate Electrolytes Using Sodium Amalgam Electrodes, by James N. Butler, Philomena T. Hsu, and John C. Synnott, *J. Phys. Chem.*, 71, 910 (1967).
2. Activity Coefficient Measurements in Aqueous NaCl-LiCl and NaCl-KCl Electrolytes Using Sodium Amalgam Electrodes by James N. Butler, Rima Huston, and Philomena T. Hsu, *J. Phys. Chem.*, 71, 3294 (1967).
3. Activity Coefficient Measurements in Aqueous NaCl-CaCl<sub>2</sub> and NaCl-MgCl<sub>2</sub> Electrolytes Using Sodium Amalgam Electrodes, by James N. Butler and Rima Huston, *J. Phys. Chem.*, 71, 4479 (1967).
4. The Standard Potential of the Calcium Amalgam Electrode, by James N. Butler, *J. Electroanal. Chem.*, 17, 309 (1968).
5. The Mean Activity Coefficient of Na<sub>2</sub>SO<sub>4</sub> in Aqueous Na<sub>2</sub>SO<sub>4</sub>-NaCl Electrolytes, by John C. Synnott and James N. Butler, *J. Phys. Chem.*, 72, 2474 (1968).
6. The Thermodynamic Activity of Calcium Ion in Sodium Chloride-Calcium Chloride Electrolytes, by James N. Butler, *Biophysical Journal*, 8, 1426 (1968).
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14. Activity Coefficients and Ion Pairs in the Systems NaCl-NaHCO<sub>3</sub>-H<sub>2</sub>O, by J. N. Butler and R. Huston, J. Phys. Chem., 74, 2976 (1970). (This paper was also presented at the Symposium on Metal Ions in Aqueous Environment, American Chemical Society National Meeting, New York, September 1969.)
15. Potentiometric Studies of Activity Coefficients in the NaCl-NaF-H<sub>2</sub>O System Using the Lanthanum Fluoride Membrane Electrode, by J. N. Butler and R. Huston, Anal. Chem., September (1970).
16. Activity Coefficients and Equilibria of Carbonates in Multicomponent Electrolytes. James N. Butler, Rima Huston, and John C. Symcott. Presented to the American Chemical Society, Harned Memorial Symposium, Chicago, September 1970. Abstract No. 16, Division of Physical Chemistry.